

LiMn_{2-x}Co_xO₄ POWDERS SYNTHESIZED BY THE MICROWAVE-INDUCED COMBUSTION METHOD AND ITS ELECTROCHEMICAL PROPERTIES

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Abstract. Spinel LiMn_{2-x}Co_xO₄ (0 ≤ x ≤ 0.20) powders with small and uniform particle size were successfully synthesized by microwave-induced combustion, which used lithium nitrate, manganese nitrate, cobalt nitrate, and urea as the starting materials. The LiMn_{2-x}Co_xO₄ powders synthesized by microwave-induced combustion were investigated by x-ray diffractometer (XRD). The LiMn_{2-x}Co_xO₄ samples were used as cathode materials for lithium-ion battery, which their discharge capacity and electrochemical characteristic properties in terms of cycle performance were also discussed in this paper. The results revealed that the LiMn₂O₄ cell synthesized by microwave-induced combustion provided a high initial capacity of 133 mAh/g and excellent reversibility compared to solid-state reaction. In addition, the Li/LiMn_{2-x}Co_xO₄ cells with excellent capacity and reversibility were attributed to dope Cr stability of the spinel structure.

1. INTRODUCTION

The spinel-type LiMn₂O₄ is an attractive cathode material for lithium ion rechargeable batteries with its relative low cost and high capacity [1-3]. However, LiMn₂O₄ 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 (700 °C to 900 °C). 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 a series of Co doped LiMn_{2-x}Co_xO₄ powders. Microwave processing of materials is 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 sample surfaces [11,12].

2. EXPERIMENTAL PROCEDURE

The synthesis process of LiMn_{2-x}Co_xO₄ 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 ni-

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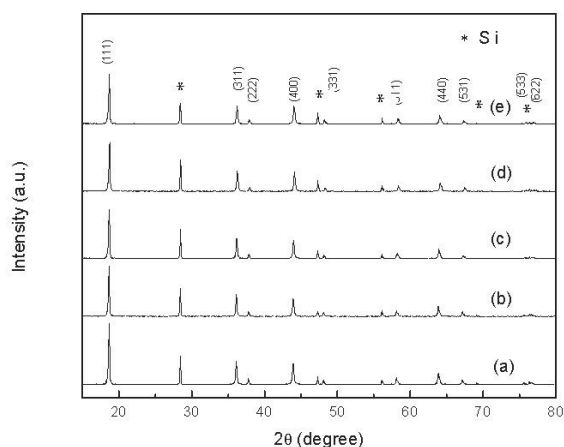


Fig. 1. XRD patterns of spinel $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ powders for (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, and (g) $x = 0.20$ prepared by microwave-induced combustion and annealing at 800°C for 8 h.

trate, 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 [$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], 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 atomic ratios of $(\text{Mn}+\text{Co})/\text{Li}$ were set to be 2. 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 $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ powders in the microwave oven took only 30 min, and then the microwave-heated $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ powders were annealed at the temperature of 800°C for 8 h in air.

The crystallography of samples were characterized using a computer-interface X-ray powder diffractometer (XRD; Rigaku D/Max-II) with $\text{CuK}\alpha$ radiation. The lattice constants were calculated by iterative least square refinements using silicon as an internal standard (10 wt.%).

The charge and discharge characteristic of $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cathode were examined in laboratory cells. The cells consist of a cathode and a lithium metal anode separated by a micro-porous polypro-

pylene separator. The electrolyte used 1M 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 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 mA/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 mV/s between 3.0-4.5 V. All assembling of the cell was carried out in a glove box filled with Ar gas.

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of the microwave-heated $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ ($0 \leq x \leq 0.20$) powders annealed at 800°C for 8 h. It is evident that the microwave-heated $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ ($0 \leq x \leq 0.20$) powders annealed at 800°C for 8 h contained the spinel phase with a space group $\text{Fd}3\text{m}$, where lithium ions occupy the tetrahedral sites (8a); Mn^{3+} and Mn^{4+} ions reside at the octahedral sites (16d); and O^{2-} ions are located at 32e sites [14]. No obvious difference could be found among the XRD patterns of $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ powders with various compositions. Such excellent structural stability provides excellent performance for $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells that we will discuss in later.

The variation in lattice parameter and average valence of Mn ion, as a function of x values for microwave-heated $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ powders annealing at 800°C is plotted in Fig. 2. It can be clearly observed that the average valence of Mn ion increases from 3.498 to 3.595 as x values increase from 0 to 0.20. This was due to the partial Mn^{3+} ions were substituted by Co^{2+} . Therefore, a slightly lower Mn^{3+} content and higher Mn^{4+} content appeared at Co-doped spinel samples, and the average valence of Mn ions in Co-doping spinel samples were higher than 3.5. This behavior will suppress the Jahn-Teller distortion for $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells during many cycles of charge and discharge. On the other hand, the lattice constant decreases from 8.250 to 8.218 as x values increase from 0 to 0.20. This was ascribed to two reasons: (1) the larger radius for Mn^{3+} ions (0.72 \AA) is large than Mn^{4+} ion (0.67 \AA). (2) Mn-Mn and Mn-O interatomic distance decreases with increasing Co content. Therefore, a higher Co content is accompanied with lower lattice constant and higher average valence of Mn ions.

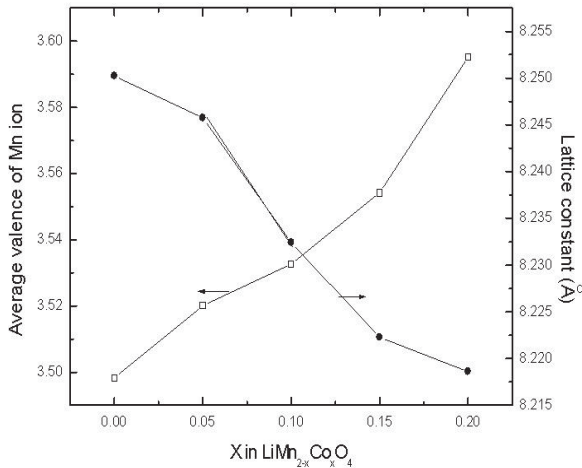


Fig. 2. The lattice parameter and average valence of Mn ion for $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ powders with various Co content.

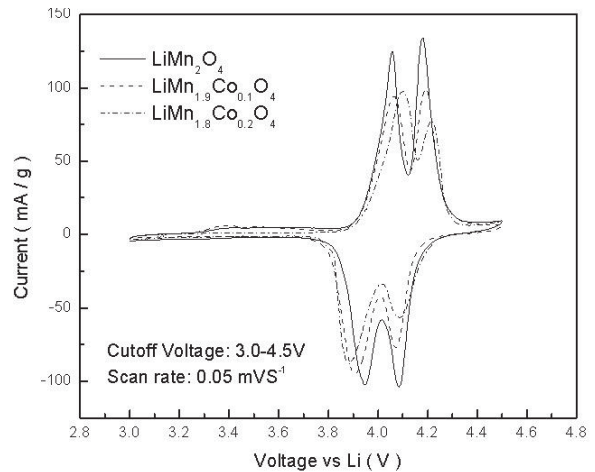


Fig. 3. Cyclic voltammogram over the potential 3.0 to 4.5 V for LiMn_2O_4 , $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$, and $\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$ at a scan rate of 0.05 mV/s.

The performance of $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ as the cathode of the lithium-ion battery was examined as follows. Fig. 3 shows the cyclic voltammogram of $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cell with $x = 0, 0.10$, and 0.20 at a sweep rate of 0.05 mV/s. The current-voltage curve clearly demonstrated the reversibility of this material upon deintercalation and intercalation of Li^+ over the range of 3.0 to 4.5V vs. Li/Li^+ . It can be clearly seen that all samples revealed two pairs of redox peaks in cyclic voltammogram, indicated lithium ions are extracted and inserted into spinel $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ by a two-step process. In addition, the two characteristic peaks of the spinel can be distinguished for small amount of Co content, which also suggested that a small amount of Co content does not disturb the spinel structure. This structural stability was

consistent with XRD results. For LiMn_2O_4 , two anodic peaks were observed at 4.09 and 4.18 V. on the other hand, $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells with $x = 0.10$ and 0.20 , which the anodic peaks became smaller, broader, and shifted toward higher potential. As shown in Fig. 3, as increasing the Co concentration causes two peaks to tend to merge into one peak. These results suggest that the stability of the $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells increased and the capacity fade decreased, as compared to the pure spinel $\text{Li}/\text{LiMn}_2\text{O}_4$ cell.

The relationship between the discharge capacity and the cycle number are plotted in Fig. 4 for $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells at a current rate of 0.1 mA between 3.0 to 4.5 V with various Co contents operated at room temperature. As can be seen, with

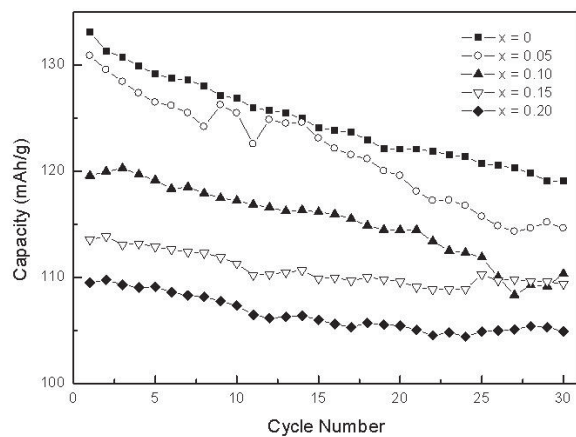


Fig. 4. Relationships between the capacity and cycle number of the $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells prepared by microwave-induced combustion.

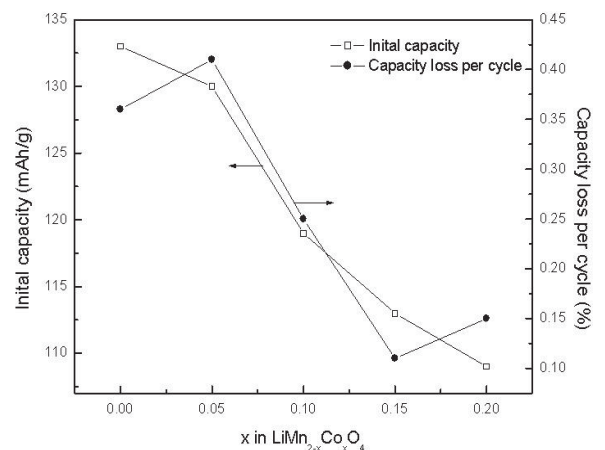


Fig. 5. Initial capacity and capacity loss per cycle as function of Co content in $\text{Li}/\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ cells.

increasing the Co content in the Li/LiMn_{2-x}Co_xO₄ cells, the initial capacity decreased gradually. On the other hand, the discharge capacity fading of the Li/LiMn_{2-x}Co_xO₄ cells with $x = 0.05$ was the most severe among these cells in spite of the high initial capacity. The relation among capacity loss per cycle, initial capacity, and Co content can be more clearly seen in Fig.5. The discharge capacity loss per cycle of the cells using Li/LiMn_{2-x}Co_xO₄ cells with $x = 0.05$ had maximum value (0.41%). On the other hand, when the Co content in LiMn_{2-x}Co_xO₄ with $x = 0.15$, capacity loss per cycle reached a minimum (0.11%), With a further increased in Co content, the capacity loss per cycle showed a slightly increased. The initial capacity for the Li/LiMn_{2-x}O₄ cell had the largest value (133 mAh/g) than the other compositions. When increasing the Co content for Li/LiMn_{2-x}Co_xO₄ cells, the initial capacity decreased gradually. When the Co content in Li/LiMn_{2-x}Co_xO₄ cells with $x = 0.20$, the initial capacity reached a minimum (109 mAh/g).

The improvement in cycle performance following the partial replacement of Mn with Co can be attributed to the stabilization of the spinel structure. This is due to the fact that bonding energy of Co-O (1067 kJ/mol) is larger than Mn-O (946 kJ/mol). Moreover, the stronger Co-O bond can stabilize the spinel structure by assisting retention of the local symmetry during cycling.

In summary, the LiMn_{2-x}Co_xO₄ powders prepared by microwave-induced combustion processing and appropriated heating treatment with excellent initial capacity and reversible properties for lithium-ion battery. These results may be due to the LiMn_{2-x}Co_xO₄ powders with ultrafine, uniform and narrow particle size distribution.

4. CONCLUSIONS

Using lithium nitrite, manganese nitrate, cobalt nitrate, and urea as the starting materials, ultrafine LiMn_{2-x}Co_xO₄ powders have been synthesized successfully by microwave-induced combustion. The results revealed the initial capacity of Li/LiMn_{2-x}Co_xO₄ cells decreased with increasing Co-doping amount. However, the capacity fading was also decreased,

which indicated that the cycle performance of Li/LiMn_{2-x}O₄ cells can be significantly improved by appropriated Co-doping. These are ascribed to Co-doping suppress the Jahn-Teller effect in spinel structure.

Spinel LiMn_{2-x}Co_xO₄ powders can be obtained by the microwave-induced combustion method in a short time, moreover the current capacity and cycle performance were comparable to those prepared by solid-state reaction and can be used as cathode material for lithium-ion battery.

REFERENCES

- [1] S. Komaba, K. Oikawa, S.-T. Myung, N. Kumagai and T. Kamiyana // *Solid State Ionics* **149** (2002) 47.
- [2] D. Song, H. Ikuta, T. Uchida and M. Wakihara // *Solid State Ionics* **117** (1999) 151.
- [3] L. Zhang, H. Noguchi and M. Yoshio // *J. Power Sources* **110** (2002) 57.
- [4] R.J. Gummow, A. de Kock and M. Wakihara // *Solid State Ionics* **69** (1994) 59.
- [5] Y. Xia, Y. Zhou and M. Yoshio // *J. Electrochem. Soc.* **144** (1997) 2593.
- [6] S.-T. Myung, S. Komaba and N. Kumagai // *J. Electrochem. Soc.* **148** (2001) A482.
- [7] P. Arora, B.N. Popov and R.E. White // *J. Electrochem. Soc.* **145** (1998) 807.
- [8] L. Guohua, H. Ikuta, T. Uchida and M. Wakihara // *J. Electrochem. Soc.* **143** (1996) 178.
- [9] K. Amine, H. Tukamoto, H. Yasuda and Y. Fujita // *J. Power Source* **68** (1997) 604.
- [10] B. Banov, Y. Todorov, A. Trifonova, A. Momchilov and V. Manev // *J. Power Sources* **68** (1997) 578.
- [11] D.E. Clark and W.H. Sutton // *Ann. Rev. Mater. Sci.* **26** (1996) 299.
- [12] O. A. Lopez, J. McKittrick and L.E. Shea // *J. Lumin.* **71** (1997) 1.
- [13] S. R. Jain, K. C. Adiga Verneker and V.R.Pai // *Comb. Flam.* **40** (1981) 71.
- [14] P. Arora, B. N. Popov and R.E. White // *J. Electrochem. Soc.* **145** (1998) 807.