LiMn$_{2-x}$Co$_x$O$_4$ POWDERS SYNTHESIZED BY THE MICROWAVE-INDUCED COMBUSTION METHOD AND ITS ELECTROCHEMICAL PROPERTIES

Yen-Pei Fu$^1$, Yu-Hsiu Su$^2$ and Cheng-Hsiung Lin$^1$

$^1$Department of Chemical Engineering, Wu-Feng Institute of Technology, Ming-Hsiung, Chiayi, Taiwan 621, R.O.C.
$^2$Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu, Taiwan 300, R.O.C.

Received: June 29, 2003

Abstract. Spinel LiMn$_{2-x}$Co$_x$O$_4$ (0 $\leq$ x $\leq$ 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$_x$O$_4$ powders synthesized by microwave-induced combustion were investigated by x-ray diffractometer (XRD). The LiMn$_{2-x}$Co$_x$O$_4$ 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 LiMn$_2$O$_4$ 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$_x$O$_4$ cells with excellent capacity and reversibility were attributed to dope Cr stability of the spinel structure.

1. INTRODUCTION

The spinel-type LiMn$_2$O$_4$ is an attractive cathode material for lithium ion rechargeable batteries with its relative low cost and high capacity [1-3]. However, LiMn$_2$O$_4$ 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 (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 serious of Co doped LiMn$_{2-x}$Co$_x$O$_4$ 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$_x$O$_4$ 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-
pylene separator. The electrolyte used 1M LiPF<sub>6</sub> 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.% polyvinylidene fluoride (PVDF). The mixture was pressed onto a stainless screen mesh at 250 kg/cm<sup>2</sup> 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<sup>2</sup> at room temperature. Cyclic voltammetry was performed for the solid solution using a flooded three-electrode glass cell. The cyclic voltammograms 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 LiMn<sub>2+x</sub>Co<sub>1-x</sub>O<sub>4</sub> (0 ≤ x ≤ 0.20) powders annealed at 800 °C for 8 h. It is evident that the microwave-heated LiMn<sub>2+x</sub>Co<sub>1-x</sub>O<sub>4</sub> (0 ≤ x ≤ 0.20) powders annealed at 800 °C for 8 h contained the spinel phase with a space group Fd3m, where lithium ions occupy the tetrahedral sites (8a); Mn<sup>2+</sup> and Mn<sup>4+</sup> ions reside at the octahedral sites (16d); and O<sup>2-</sup> ions are located at 32e sites [14]. However, it is possible that the difference could be found among the XRD patterns of LiMn<sub>2+x</sub>Co<sub>1-x</sub>O<sub>4</sub> powders with various compositions. Such excellent structural stability provides excellent performance for Li/LiMn<sub>2+x</sub>Co<sub>1-x</sub>O<sub>4</sub> cells that we will discuss in detail later.

The variation in lattice parameter and average valence of Mn ion, as a function of x values for microwave-heated LiMn<sub>2+x</sub>Co<sub>1-x</sub>O<sub>4</sub> powders annealed 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<sup>2+</sup> ions were substituted by Co<sup>2+</sup>. Therefore, a slightly lower Mn<sup>3+</sup> content and higher Mn<sup>4+</sup> 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 Li/LiMn<sub>2+x</sub>Co<sub>1-x</sub>O<sub>4</sub> 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<sup>3+</sup> ions (0.72 Å) is larger than Mn<sup>4+</sup> ion (0.67 Å). (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.
The performance of LiMn$_{2-x}$Co$_x$O$_4$ as the cathode of the lithium-ion battery was examined as follows. Fig. 3 shows the cyclic voltammogram of LiMn$_{2-x}$Co$_x$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 4.5 V vs. Li/Li$^+$. It is 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 LiMn$_{2-x}$Co$_x$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$_{2-x}$O$_4$, two anodic peaks were observed at 4.09 and 4.18 V, on the other hand, Li/LiMn$_{2-x}$Co$_x$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. There results suggest that the stability of the Li/LiMn$_{2-x}$Co$_x$O$_4$ cells increased and the capacity fade decreased, as compared to the pure spinel Li/LiMn$_{2-x}$O$_4$ cell.

The relationship between the discharge capacity and the cycle number are plotted in Fig. 4 for Li/LiMn$_{2-x}$Co$_x$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
increasing the Co content in the Li/Li$_{2x}$Mn$_{2-x}$CoO$_2$ cells, the initial capacity decreased gradually. On the other hand, the discharge capacity fading of the Li/Li$_{2x}$Mn$_{2-x}$CoO$_2$ 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/Li$_{2x}$Mn$_{2-x}$CoO$_2$ cells with $x = 0.05$ had maximum value (0.41%). On the other hand, when the Co content in Li$_{2x}$Mn$_{2-x}$CoO$_2$ 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/Li$_2$MnO$_2$ cell had the largest value (133 mAh/g) than the other compositions. When increasing the Co content for Li/Li$_{2x}$Mn$_{2-x}$CoO$_2$ cells, the initial capacity decreased gradually. When the Co content in Li/Li$_{2x}$Mn$_{2-x}$CoO$_2$ 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 Li$_{2x}$Mn$_{2-x}$CoO$_2$ 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 Li$_{2x}$Mn$_{2-x}$CoO$_2$ powders with ultafine, uniform and narrow particle size distribution.

4. CONCLUSIONS

Using lithium nitrate, manganese nitrate, cobalt nitrate, and urea as the starting materials, ultafine Li$_{2x}$Mn$_{2-x}$CoO$_2$ powders have been synthesized successfally by microwave-induced combustion. The results revealed he initial capacity of Li/Li$_{2x}$Mn$_{2-x}$CoO$_2$ cells decreased with increasing Co-doping amount. However, the capacity fading was also decreased, which indicated that the cycle performance of Li/Li$_{2x}$Mn$_{2-x}$CoO$_2$ cells can be significantly improved by appropriated Co-doping. These are ascribe to Co-doping suppress the Jahn-Teller effect in spinel structure.

Spinel Li$_{2x}$Mn$_{2-x}$CoO$_2$ 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