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Comparison of the microwave-induced combustion and solid-state reaction for the synthesis of $LiMn_2O_4$ powder and their electrochemical properties

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Abstract

In the current research, we proposed a new method called microwave-induced combustion synthesis to produce $LiMn_2O_4$ powders. The microwave-induced combustion synthesis entails the dissolution of metal nitrates, and urea in water, and then heating the resulting solution in a microwave oven. Spinel $LiMn_2O_4$ powders were successfully synthesized by microwave-induced combustion. The microwave-heated $LiMn_2O_4$ powders annealed at various temperatures in the range of 600–800 °C were determined. The resultant powders were characterized by X-ray diffractometer (XRD), and scanning electron microscopy (SEM). The annealed samples were used as cathode materials for lithium-ion battery, for which their discharge capacity and electrochemical characteristic properties in terms of cycle performance were also investigated. The $LiMn_2O_4$ cell provides a high initial capacity of 133 mAh/g and excellent reversibility. The excellent capacity and reversibility were attributed to $LiMn_2O_4$ powders with small and uniform particle size produced by microwave-induced combustion synthesis.

Keywords: A. Microwave Processing; A. Powders: Chemical preparation; E. Batteries

1. Introduction

Recently, the spinel-type $LiMn_2O_4$ has became quite attractive as 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, Cr, Co [8–10]. 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. 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 $LiMn_2O_4$ 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]. The microwave-induced combustion synthesis entails the dissolution of lithium nitrate, manganese nitrate and urea in water, and then heating the resulting solution in a microwave oven. Urea and metal nitrate decompose 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 reaction is not complete until all the flammable substances are all burnt out and it turns out to be a loose substance containing voids, pores, and highly friable material formed by the escaping gases

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during the combustion reaction [12]. The whole process takes only 30 min to yield $LiMn_2O_4$ powders.

2. Experimental

2.1. Preparation of $LiMn_2O_4$ powders

2.1.1. Microwave-induced combustion

The synthesis process of $LiMn_2O_4$ 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 nitrate, and urea was based on the total oxidizing and reducing valences of the oxidizer and fuel using the concepts in propellant chemistry [13].

Stoichiometric amounts of lithium nitrate [$LiNO_3$], manganese nitrate [$Mn(NO_3)_2\cdot 6H_2O$], and urea [$CO(NH_2)_2$] were dissolved in 15 ml of water in a crucible. The atomic ratios of Mn/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 volatilities instantly leaving behind a solid mass above 1000 °C. The entire combustion process for producing $LiMn_2O_4$ powders in the microwave oven took only 30 min, and then the microwave-heated $LiMn_2O_4$ powders were annealed in the temperature range of 600–800 °C for 8 h in air.

2.1.2. Solid-state reaction

The $LiMn_2O_4$ powders were also prepared by the solid-state reaction from stoichiometric mixture of $LiCO_3$ and $MnCO_3$. The mixtures were preheated at 800 °C for 8 h and ground after cooling, then heated at 800 °C for 24 h in air.

2.2. Characterization

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 °C/min from room temperature to 1000 °C in air was employed. The crystal structure of samples was determined using a computer-interface X-ray powder diffractometer (XRD; Rigaku D/Max-II) with Cu Kα radiation. The lattice constants were calculated against silicon standard (10 wt%). The total average valences of Mn ion were obtained by potential titration method. Firstly, the $LiMn_2O_4$ 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. $N_4P_2O_7$ was added to complex the oxidation product Mn^{3+}. The average oxidation state of Mn was calculated by above-mentioned method [14]. The particle morphology and size of the microwave-heated $LiMn_2O_4$ powders and annealed at various temperatures were characterized using a scanning electron microscopy (SEM; JEOL JSM-6500F).

The charge and discharge characteristics of $LiMn_2O_4$ 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 LiPF6 in a 50/50 vol% mixture of EC/DMC. The positive electrode was consisted of a mixture of 83 wt% of $LiMn_2O_4$, 10 wt% of acetylene black, and 7 wt% poly vinylidene fluoride (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 an oven. The cells were cycled in the voltage range of 3–4.5 V with typical current density 0.1 and 0.3 mA/cm^2, respectively, 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 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 step from room temperature to 200 °C may be attributed to the evaporation of residual water; whereas the second step between 250 and 420 °C corresponds to the formation of $LiMn_2O_4$ phase; the third step above 450 °C, which indicates a weight loss of 3% of residual carbonates. 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 continued decomposition of reactants and formation of $LiMn_2O_4$.

Fig. 2 shows the X-ray diffraction patterns of the microwave-heated $LiMn_2O_4$ powders and the microwave-

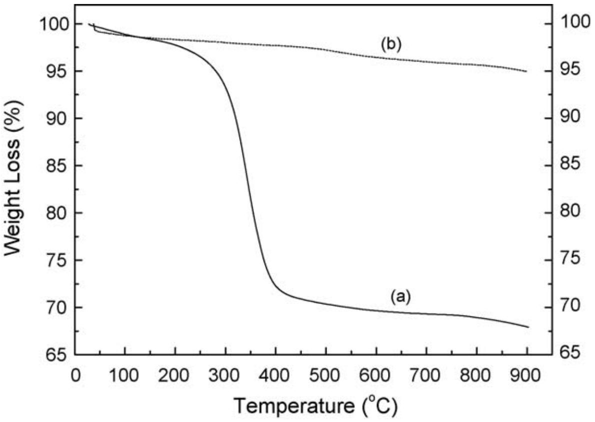

Fig. 1. The thermogravimetric analysis curves for (a) the mixtures of the reactants $LiCO_3$ with $MnCO_3$ powders and (b) the microwave-heated $LiMn_2O_4$ powders.

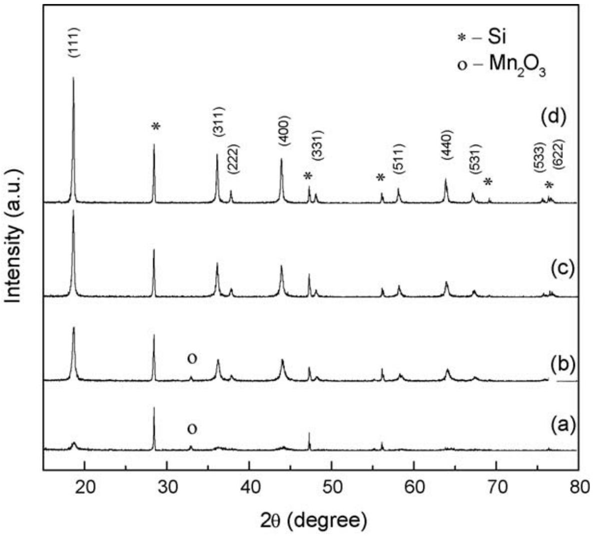

Fig. 2. X-ray diffraction patterns of the microwave-heated $LiMn_2O_4$ powders annealed at various temperatures (a) as-received, (b) annealed at 600 °C for 8 h, (c) annealed at 700 °C for 8 h, and (d) annealed at 800 °C for 8 h.

heated $LiMn_2O_4$ powders annealed at various temperatures. It is evident that the microwave-heated $LiMn_2O_4$ powders contained the spinel $LiMn_2O_4$ phase and Mn_2O_3 phase. The formation of impurity phase (Mn_2O_3) indicated that the temperature is not high enough to reach full crystallization and containing some vacancies in $LiMn_2O_4$ structure during combustion. Therefore, the microwave-heated $LiMn_2O_4$ powders required further thermal treatment. For the microwave-heated $LiMn_2O_4$ powders annealed at 700 °C, the Mn_2O_3 phase disappears and well-crystallized-$LiMn_2O_4$ peaks appear with a space group *Fd*3*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 [7]. As expected, the crystallization of $LiMn_2O_4$ is further enhanced when the annealing temperature is raised above 700 °C.

Fig. 3 presents the morphology of the microwave-heated $LiMn_2O_4$ powders and the microwave-heated specimens annealed at various temperatures for 8 h. As shown in Fig. 3(a), the microwave-heated $LiMn_2O_4$ powders have nano-size particle. Fig. 3(b) and (c) shows the microwave-heated $LiMn_2O_4$ powders annealed at 600 °C and 700 °C, and the particle sizes of these samples are still less than 0.1 μm. As shown in Fig. 3(d), the microwave-heated $LiMn_2O_4$ powders annealed at 800 °C has a uniform and narrow particle size distribution with regular particle shape about 0.25 μm. According to Fig. 3 results, the particle size increases with rising the annealing temperature from 600 to 800 °C.

Heat treatment conditions and the average valence of Mn ion for microwave-heated $LiMn_2O_4$ powders before assembling for cells were presented in Table 1. The variation in lattice parameter and average valence of Mn ion, as a function of the microwave-heated $LiMn_2O_4$ powders annealing temperature plots in Fig. 4. The average valence of Mn ion decreases from 3.543 to 3.498 as the annealing temperature increases from 600 to 800 °C. This is due to the oxygen loss at high temperature accompanied with the side reaction $Mn^{4+} \rightarrow Mn^{3+}$ [15]. Therefore, a slight higher Mn^{3+} content and lower Mn^{4+}

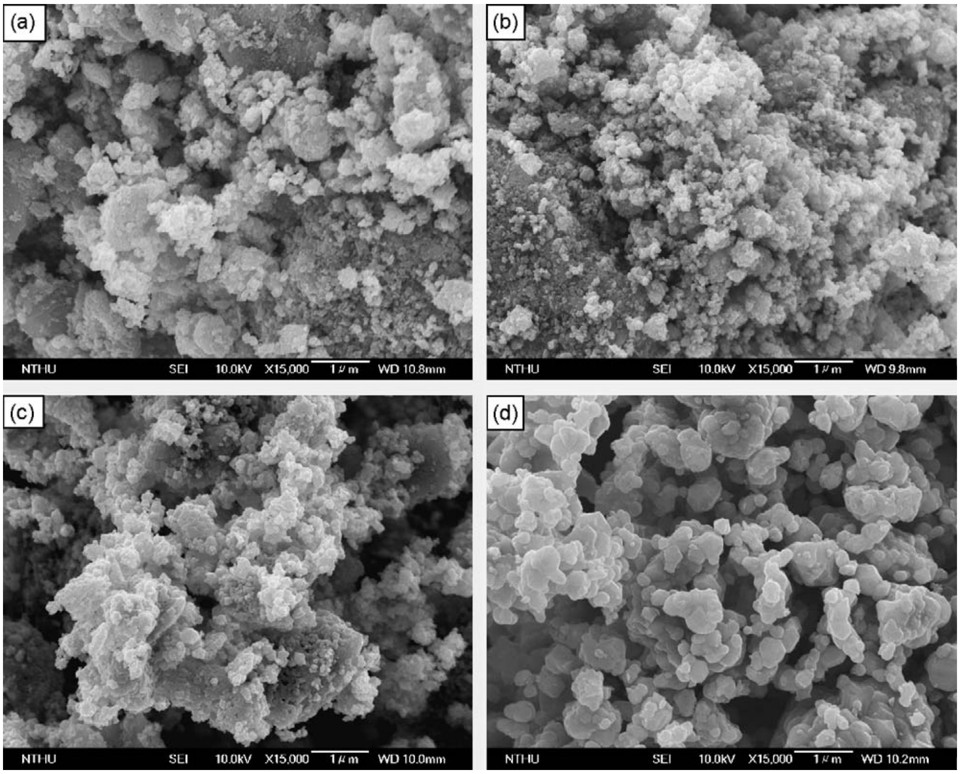

Fig. 3. SEM photographs of the microwave-heated $LiMn_2O_4$ powders: (a) as-received, (b) annealed at 600 °C for 8 h, (c) annealed at 700 °C for 8 h, and (d) annealed at 800 °C for 8 h.

Table 1
Heat treatment conditions and the average valence of Mn ion for microwave-heated $LiMn_2O_4$ powders before assembling for cells.

Sample number	Annealing conditions	Mn average valence
A	600 °C for 8 h	3.543
B	700 °C for 8 h	3.510
C	800 °C for 8 h	3.498

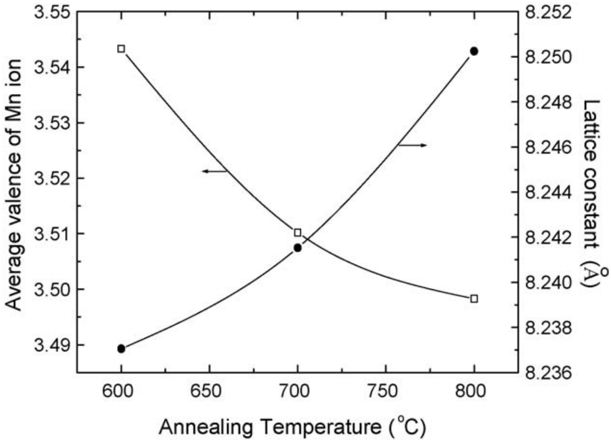

Fig. 4. The lattice parameter and average valence of Mn ion for microwave-heated $LiMn_2O_4$ powders annealing at various temperatures for 8 h.

content appears at high annealing temperatures. On the other hand, the lattice constant increases from 8.237 to 8.250 as the annealing temperature increases from 600 to 800 °C. This was due to the larger radius for Mn^{3+} ions (0.72 Å) than Mn^{4+} ion (0.67 Å). Therefore, a high Mn^{3+}/Mn^{4+} ratio is accompanied by high lattice constant at higher annealing temperatures.

3.2. Electrochemical properties

The performance of $LiMn_2O_4$ as the cathode of the lithium-ion battery was examined as follows. Fig. 5 shows the cyclic voltammogram of $LiMn_2O_4$ cell for the sample A and sample C, with 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 3.0–4.5 V vs. Li/Li^+. It is can be clearly seen that sample A and sample C both revealed two pairs of redox peaks in cyclic voltammogram, indicating lithium ions are extracted and inserted into spinel $LiMn_2O_4$ by a two step process. For sample A, two anodic peaks were observed at 4.09 and 4.18 V on the other hand, the sample C, which the anodic peaks becomes larger and shift toward lower potential, which located at about 4.05 and 4.18 V, respectively.

According to Fig. 5 results, sample A had broadening peaks and lower potential than sample C, may be attributed to the poor crystallinity of sample C. The broadening of peaks in the voltammograms could also be due to an overvoltage or impedance within system [16]. In addition, the difference in potential depends on the difference in energy of the lithium ions in the tetrahedral sites, which depends on the energy of the bond between Li^+ and its neighbors [17]. In other words, removal of lithium ions from the tetrahedral sites in sample A requires more energy than in sample C.

Fig. 6 shows the first discharge curves for $Li/LiMn_2O_4$ cells operated between 3.0 and 4.5 V at a constant discharge current density of 01 mA/cm^2. For all samples, two distinct plateaus were observed on the discharge curves. This result is strongly consistent with cyclic voltammogram curve, corresponding to the electrodes undergo two stages of reversible oxidation and reduction process. Moreover, as can be seen in Fig. 5, sample C has much shaper peaks than sample A, indicating flatter discharge curve occurred at sample C. Sample A reveals two plateaus at 4.10 and 3.94 V with the current discharge capacity of 112 mAh/g, compared to sample B had two plateaus at 4.10 and 3.96 V with the current discharge capacity of 125 mAh/g and sample C had two plateaus at 4.10 and 3.97 V with the current discharge capacity of 133 mAh/g at first cycle. Sample A provided a lower initial capacity and not clear plateaus in the discharge curve. This was attributed to poor crystallinity of microwave-heated $LiMn_2O_4$ powders annealed at such low temperature. Sample C provided the highest initial capacity of 133 mAh/g in the discharge curve among all samples. This

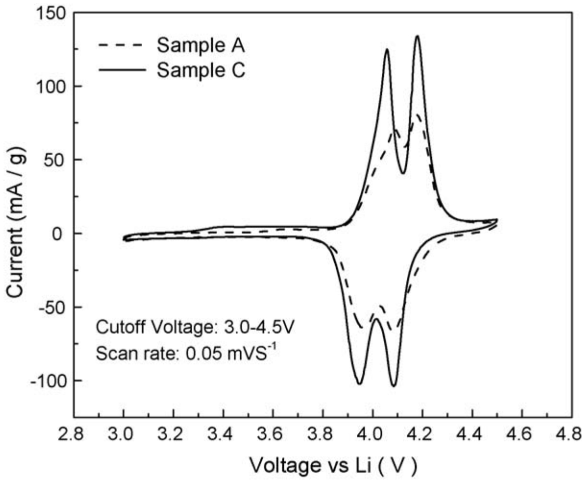

Fig. 5. Cyclic voltammogram over the potential 3.0–4.5 V for sample A and sample C at a scan rate of 0.05 mV/s.

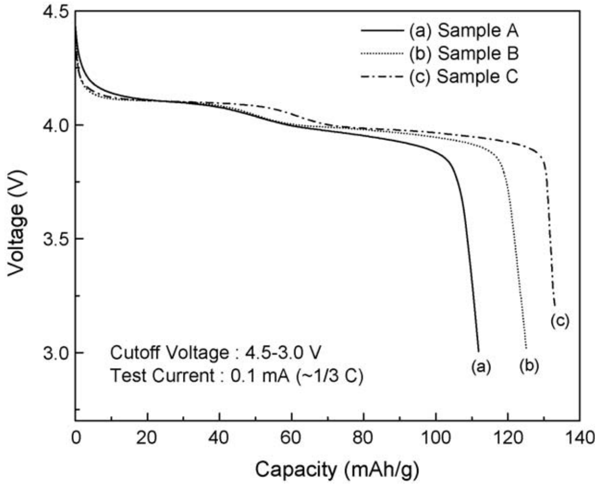

Fig. 6. The first discharge curves for (a) sample A, (b) sample B, and (c) sample C at a current rate of 0.1 mA.

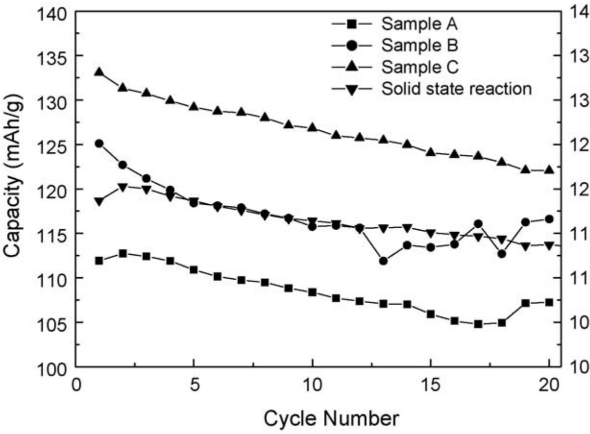

Fig. 7. The variation of discharge capacity as function of cycle number for Li/$LiMn_2O_4$ cells for sample A, sample B, sample C, and the mixture of Li_2CO_3 and $MnCO_3$ powders was preheated at 800 °C for 8 h and finally heated at 800 °C for 24 h in air.

value is comparable to the method prepared by solid-state reaction [8] or melt impregnation [18]. Therefore, the $LiMn_2O_4$ powders prepared by microwave-induced combustion method can be used as cathode active materials for lithium-ion battery.

The relationship between the discharge capacity and the cycle number is plotted in Fig. 7 for Li/$LiMn_2O_4$ cells at a current rate of 0.1 mA between 3 and 4.5 V for various samples operated at room temperature. The discharge capacity fading of the cells using sample C is a little faster than for cells using sample A and sample B. The capacity of losses for the first 20 cycles were about 4.17% of initial capacity for sample A, compared to 7.20% and 8.27% for sample B and sample C. The capacity fading of the cells using solid-state reaction, which was prepared by the mixture of Li_2CO_3 and $MnCO_3$ preheated at 800 °C for 8 h with intermittent grinding and then heated at 800 °C for 24 h in air provided the initial capacity of 118 mAh/g in the discharge curve and the capacity losses about of 4.38% for the first 20 cycles. A comparison of sample C and the solid-state reaction sample reveals that sample C with higher initial capacity shows a little faster discharge capacity fading rate for the first 20 cycles. This may be attributed to the oxygen loss and higher Mn^{3+} content appeared for the microwave-heated $LiMn_2O_4$ powders annealed at such high temperature (800 °C).

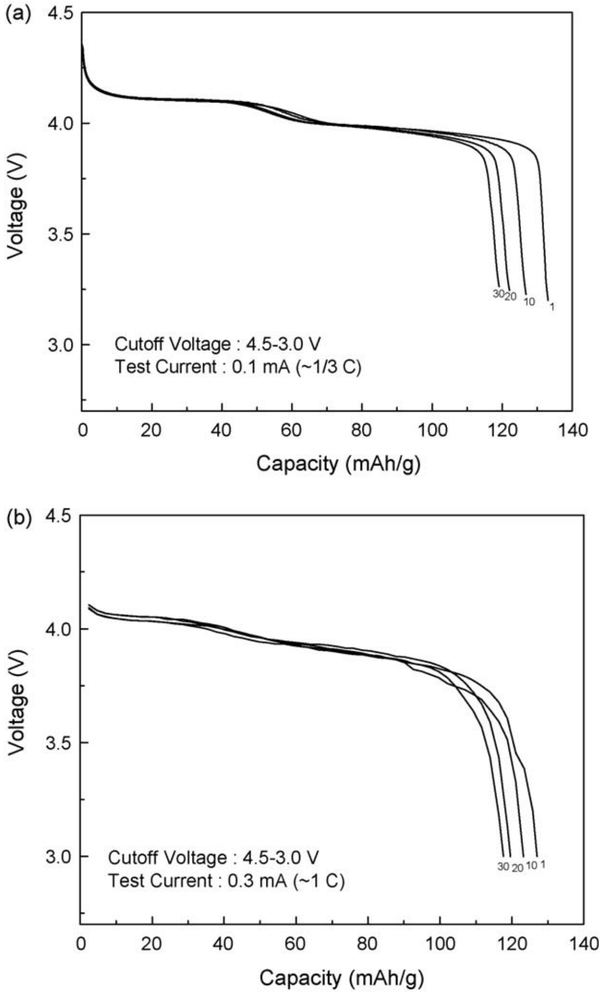

Fig. 8. The 1st, 10th, 20th, 30th, discharge curves in the voltage from 3.0 to 4.5 V at a current rate of (a) 0.1 mA and (b) 0.3 mA for sample C.

The reversibility of the stoichiometric spinel phase had been significantly improved, however in previous reports the fading capacity of the cell on cycling cannot be avoided. Xia and Yoshio [17] reported that the capacity loss occurred only on the higher voltage plateau. The 1st, 10th, 20th, and 30th discharge curves between 3.0 and 4.5 V for a Li/$LiMn_2O_4$ cell at different current rate of 0.1 and 0.3 mA for sample C are presented in Fig. 8. As shown in Fig. 8(a) at a current rate of 0.1 mA that the capacity losses of 6.24, 4.77, 2.98 mAh/g are observed between the 1st to 10th, 10th to 20th, and 20th to 30th cycle, respectively. After 30 cycles, 90% cell capacity is retained. On the other hand, the discharge curve for a Li/$LiMn_2O_4$ cell at a current rate of 0.3 mA is shown in Fig. 8(b), showing that the shape of discharge curve gradually changes from two plateaus to one plateau on cycling. However, the sample C discharged at higher current rate (0.3 mA) showed nearly the same capacity losses rate with lower current rate (0.1 mA), the capacity is retained at 93% after 30 cycles. These results indicated that the spinel $LiMn_2O_4$ powders

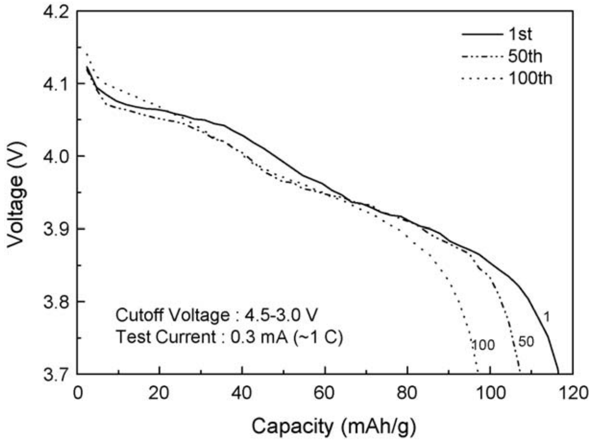

Fig. 9. The 1st, 50th, 100th discharge curves in the voltage from 3.7 to 4.2 at a current rate of 0.3 mA for sample C.

synthesized by microwave-induced combustion have relative good reversibility at a higher current rate.

In order to further study the relation between capacity and cycle number for sample C at a current rate of 0.3 mA, the 1st, 50th, 100th, discharge curves in the voltage range of 3.7–4.2 V are plotted in Fig. 9. As increased with the cycle number, the shape of two distinct plateaus was not clear gradually, while the voltage also shifted to a higher voltage for lithium insertion. This may be ascribed to two reasons: (1) the insertion of lithium from deep discharge depths after many cycles requiring higher energy than on the first discharge, (2) two phases structure is gradually transformed to one phase structure.

In summary, the $LiMn_2O_4$ powders prepared by microwave-induced combustion processing and appropriate heat treatment exhibited excellent initial capacity and reversible properties. These results may be due to the ultrafine, uniform and narrow particle size distribution.

4. Conclusions

Using lithium nitrate, manganese nitrate, and urea as the starting materials, ultrafine $LiMn_2O_4$ powders have been synthesized successfully by microwave-induced combustion. Results of this study show that annealing temperature effect greatly the electrochemical properties of $LiMn_2O_4$ samples for lithium-ion battery. Both the initial capacity and magnetization and cycle performance of $LiMn_2O_4$ cell can be significantly improved by appropriate thermal treatment for microwave-heated $LiMn_2O_4$ powders.

In order to study the electrochemical properties of the $LiMn_2O_4$ powders, which prepared by the microwave-induced combustion and appropriate heating treatment. The fabrication of lithium-ion rechargeable cells was made and the cell performances were evaluated at room temperature. Spinel $LiMn_2O_4$ powders can be obtained by the microwave-induced combustion method in a short time, while the current capacity and cycle characterization were comparable to those prepared by solid-state reaction.

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