

Short communication

LiMn_{1.95}M_{0.05}O₄ (M: Al, Co, Fe, Ni, Y) cathode materials prepared by combustion synthesis

Heon-Jin Choi^{*}, Ki-Min Lee, June-Gunn Lee

Multifunctional Ceramics Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

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Abstract

Spinel LiMn_{1.95}M_{0.05}O₄ (M: Al, Co, Fe, Ni, or Y) is prepared by a combustion synthesis, which is a simple, rapid and cost-effective process for obtaining oxide powders. The spinel is obtained by combustion of lithium hydroxide, manganese nitrate, M-nitrates, and urea at about 280°C for 1 min. Well-defined spinel LiMn_{1.95}M_{0.05}O₄ was obtained by further heat-treatment at 800°C for 10 h. The synthesized LiMn_{1.95}M_{0.05}O₄ shows lower initial capacities, viz. 90–132 mAh/g than undoped LiMn₂O₄. The latter has an initial capacity of 146 mAh/g which fades to 100 mAh/g with cycling. On the other hand, LiMn_{1.95}Co_{0.05}O₄, LiMn_{1.95}Ni_{0.05}O₄, and LiMn_{1.95}Y_{0.05}O₄ display better cycleability than LiMn₂O₄. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Spinel LiMn₂O₄ has been extensively studied as a cathode material for lithium secondary batteries due to several advantages, such as easy preparation, low cost, less toxicity, and environmental safety [1,2]. It has been usually prepared by a solid-state reaction which consists of mechanical mixing and extensive heating at high temperature. The solid-state reaction results, however, in inhomogeneity of composition, irregular grain shape and larger grain size with broad distribution. These are all features which can adversely affect the capacity and cycleability of lithium batteries.

Several synthesis processes, such as the sol–gel process [3,4], the Pechini process [5], and the emulsion-drying process [6] have been investigated for obtaining LiMn₂O₄ with homogeneous composition, spherical grain shape, and small grain size with a narrow size distribution. More recently, a combustion process has also been investigated for obtaining LiMn₂O₄ [7–9]. This process uses the combustion reaction of some oxidizers and fuels, such as glycine, citric acid, and/or urea [7–11], which emits heat and promotes a chemical reaction to form rapidly oxide

powders. In a previous study [9], we have shown that spinel LiMn₂O₄ can be obtained by a combustion reaction below 300°C within 1 min. Although, the LiMn₂O₄ thus synthesized displayed comparable electrochemical properties to those of LiMn₂O₄ synthesized by a solid-state reaction process, capacity fading was observed. It is well known that the doping of cations into LiMn₂O₄ can improve cycleability [12–15]. Accordingly, in this study, spinel LiMn_{1.95}M_{0.05}O₄ (M: Al, Co, Fe, Ni, or Y) is prepared by combustion synthesis and the electrochemical properties are characterized.

2. Experimental

Stoichiometric amounts of lithium hydroxide monohydrate (LiOH·H₂O), manganese nitrate hexahydrate (Mn(NO₂)₆·6H₂O), M-nitrates (M: Al, Co, Fe, Ni, or Y) with cationic ratio of Li:Mn:M = 1:1.95:0.05, and urea were dissolved in distilled water. The amount of urea, which corresponds to a ratio of fuel to nitrate in which the fuel can react completely with nitrate, was calculated by the method of Jain and Adiga [10]. The solution was heated at 80°C with constant stirring until a dry mixture was obtained. The dried mixture was then heated further to initiate the combustion reaction, which gives synthesized powders (denoted as CM (M: Al, Co, Fe, Ni, or Y)) within

^{*} Corresponding author. Fax: +82-2-958-5509.
E-mail address: hjchoi@kist.re.kr (H.-J. Choi).

1 min. The powders were subsequently heat-treated at 800°C for 12 h in air (denoted as HTC_M) for developing the crystallinity of the spinel $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$. Thermogravimetric analysis (TGA) and differential thermal analysis (DSC) were performed to analyze the thermal behavior of the mixtures and the synthesized powders. The phases of the synthesized powders were determined by X-ray diffractometry (XRD). The morphology and size of the powders were observed by scanning electron microscopy (SEM). The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method. The electrochemical properties of $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ powders were characterized in $\text{Li}/\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ cells. The cathode was made by mixing the synthesized $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ (85 wt.%), acetylene

black (9 wt.%) as a conducting agent, and poly(vinylidene fluoride) (6 wt.%) emulsion with *N*-methyl-2-pyrrolidone into slurry. The reference and counter electrodes consisted of thin Li sheet pressed on to a copper grid. The electrolyte was 1:1 ethylene carbonate:dimethyl carbonate solvent containing 1 M LiPF_6 . The cells were cycled between cut-off voltages of 3.3 and 4.3 $\text{V}_{\text{Li}/\text{Li}^+}$, where the *C*-rate was 1/5*C*.

3. Results and discussion

In a previous study [9], we investigated the thermal behavior of a mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_2)\cdot 6\text{H}_2\text{O}$, and

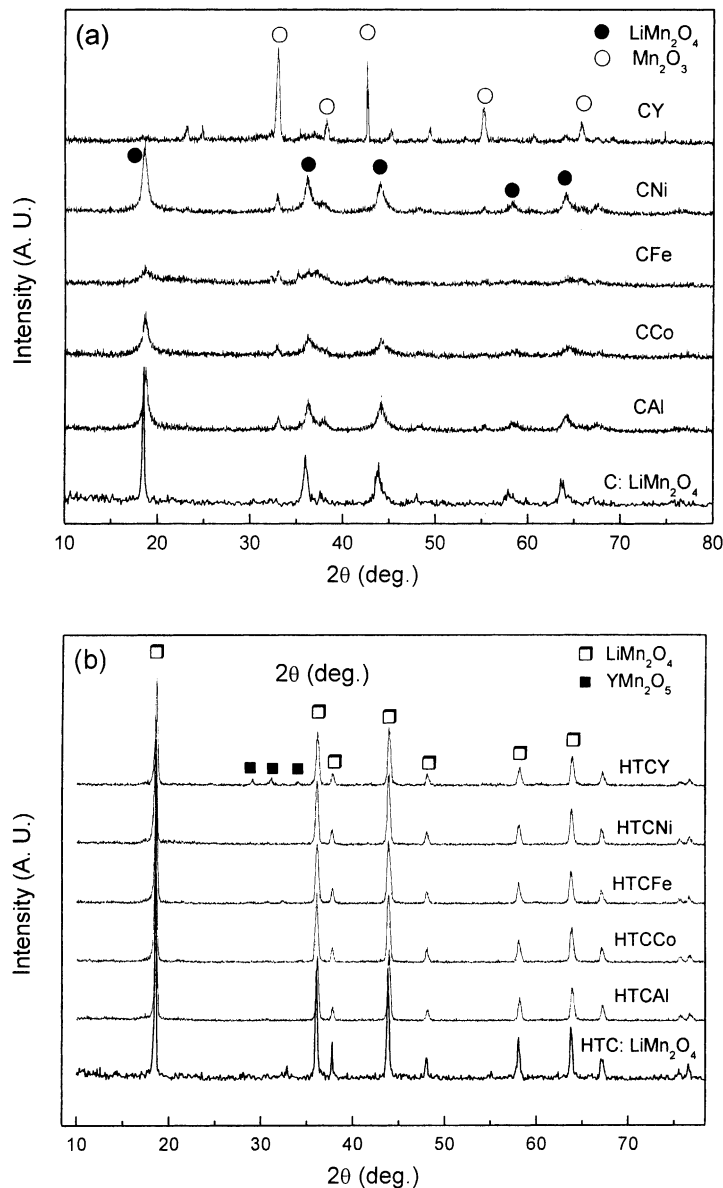


Fig. 1. XRD patterns of $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ synthesized by (a) combustion, and (b) combustion and further heat-treatment at 800°C for 12 h.

urea by TGA and DSC. The results showed a weight loss and an exothermic peak at 280°C, which is associated with the redox reactions of the chemical groups in urea. Further weight loss and exothermic or endothermic peaks were not observed at higher temperature. This suggests that the combustion reaction occurs around 280°C and the TGA–DSC curves of the as-combustion synthesized LiMn_2O_4 confirmed that the reaction was completed in 1 min. The absence of a weight loss and exothermic or endothermic peaks indicate the formation of pure spinel LiMn_2O_4 . The addition of a small amount of M-nitrate to the $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_2)\cdot 6\text{H}_2\text{O}$, and urea mixture exerted

little effect on the thermal behavior of the mixture. It is therefore concluded that the combustion reaction of mixtures which contain M-nitrates also occurs around 280°C within 1 min.

X-ray diffraction patterns of the CM powders are shown in Fig. 1(a). Peaks for the spinel LiMn_2O_4 single phase are detected for the mixtures without M-nitrate (denoted as C in Fig. 1(a)), which indicates that the combustion reaction is sufficient to form LiMn_2O_4 . The addition of M-nitrate retards the combustion reaction and results in the formation of LiMn_2O_4 as the major phase and Mn_2O_3 as a minor phase. For CY powders, however, Mn_2O_3 appeared as the major

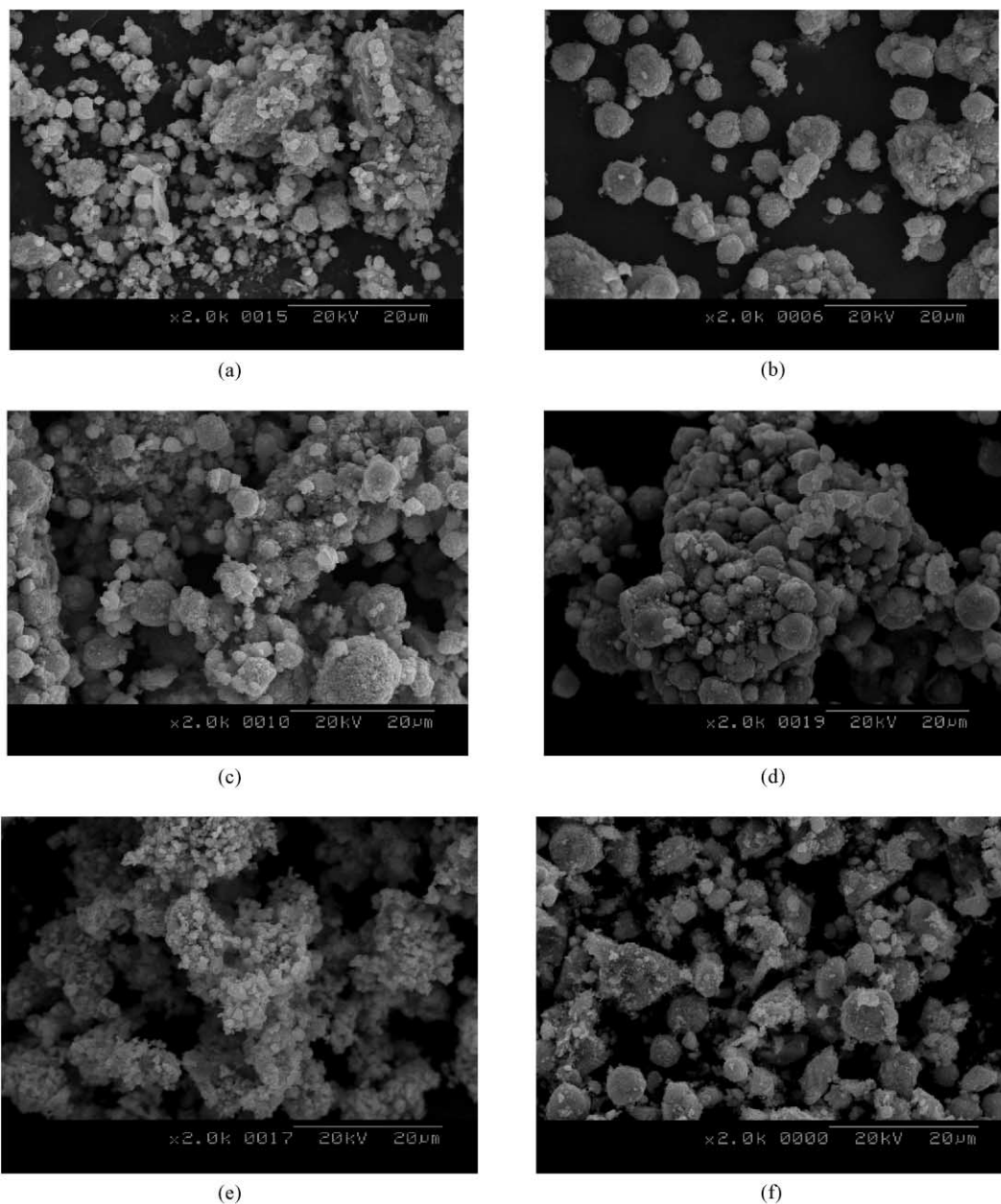


Fig. 2. Electron micrographs of $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ synthesized by combustion process: (a) CAI; (b) CCo; (c) CFe; (d) CNi; (e) CY; (f) without dopant.

phase. The retardation of the combustion reaction on addition of M-nitrate may relate to the differences of ionic radius of the M-cations compare with Mn^{3+} . In the combustion reaction, an M-cation with a similar ionic radius to Mn^{3+} (0.66 Å) can be incorporated into the spinel structure by substitution of Mn^{3+} . The ionic radii of Al^{3+} (0.54 Å), Co^{3+} (0.55 Å), Fe^{2+} (0.61 Å), and Ni^{2+} (0.69 Å) are similar to that of Mn^{3+} . There may, however, be lattice strain when the cation incorporates into spinel structure due to the differences in ionic radius and this may retard the formation of spinel structure. This can explain why the spinel structure has not been observed in the mixtures containing Y-nitrate. The ionic radius of Y^{3+} (0.9 Å) is much larger than that of Mn^{3+} .

The XRD patterns of the HTCМ powders which are synthesized by the combustion reaction and further heat-treatment are shown in Fig. 1(b). The XRD patterns show that the spinel LiMn_2O_4 structure develops for the HTCМ powders including HTCY, although the latter contains YMn_2O_5 as impurity phase. The sharper diffraction peaks and the narrower widths of the peaks of HTCМ powder compared with CM powders indicate that the crystallinity of the LiMn_2O_4 synthesized by combustion reaction is not fully developed, although it has well-defined spinel structure.

Scanning electron micrographs of the HTCМ powders are shown in Fig. 2. The powders consist of spherical grains of size in the range of 1–10 μm together with larger agglomerates. The typical specific surface areas of the HTCМ powders are $\sim 1.2 \text{ m}^2/\text{g}$ and are slightly smaller than those of CM powders which have typical specific surface areas of $\sim 1.4 \text{ m}^2/\text{g}$.

Plots of the discharge capacity versus the cycle number of Li/HTCМ cells are presented in Fig. 3. The cell with undoped LiMn_2O_4 (denoted as HTC in Fig. 3) yields the highest initial capacity (146 mAh/g), whereas the LiMn_2O_4 spinel powder synthesized by solid-state reaction at 800°C for 12 h by using $\gamma\text{-MnO}_2$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ (denoted as D in Fig. 3) shows a lower initial capacity of 120 mAh/g and faster capacity fading with cycling. This indicates the feasibility of the combustion process for synthesizing LiMn_2O_4 with better electrochemical properties as well as time and cost saving as compare with solid-state reaction process.

In previous studies [12–15], doping of cations in LiMn_2O_4 shows a trade-off between capacity and cycleability, i.e. doping prevents capacity fading, but decreases the initial capacity. The trade-off relationship is also observed in this study. All the HTCМ powders show lower initial capacity than undoped LiMn_2O_4 , but better cycleability. HTCCo, HTCNi, and HTCFe are particularly stable, whereas HTCAI and HTCFe exhibit capacity fading within 10 cycles. High initial capacity (125 mAh/g) and stable cycleability are found for HTCCo.

The differential plots of capacity versus voltage of undoped LiMn_2O_4 and HTCCo are given in Fig. 4. The differential plot for undoped LiMn_2O_4 displays sharp peaks at about 4.0 and 4.1 V versus Li/Li^+ and the lower voltage region, but not the higher voltage region diminishes with cycling. This suggests that Li^+ intercalation into the spinel structure is hindered by the degradation of structure with cycling [13]. By contrast, the differential plot of HTCCo shows no decrease in either the higher or the lower voltage region, which means that Co doping stabilizes the spinel structure [13].

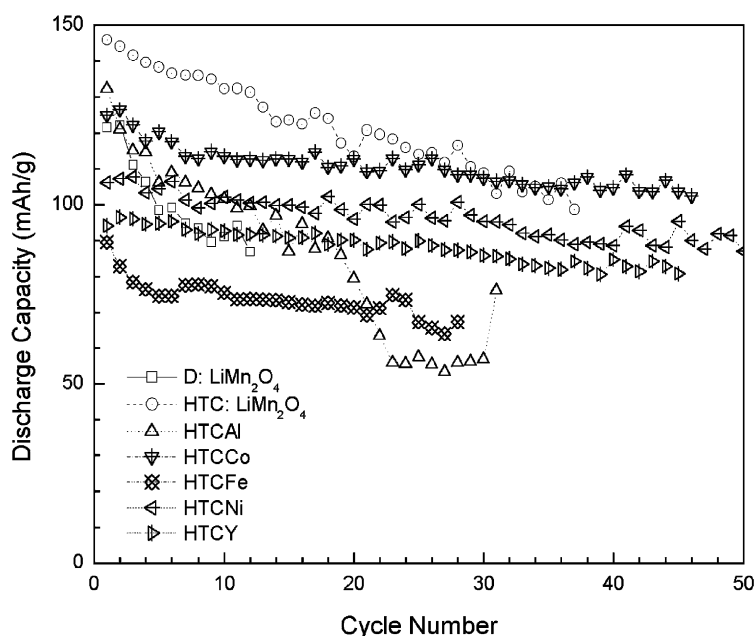


Fig. 3. Cycleability of $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ synthesized by combustion and further heat-treated at 800°C for 12 h.

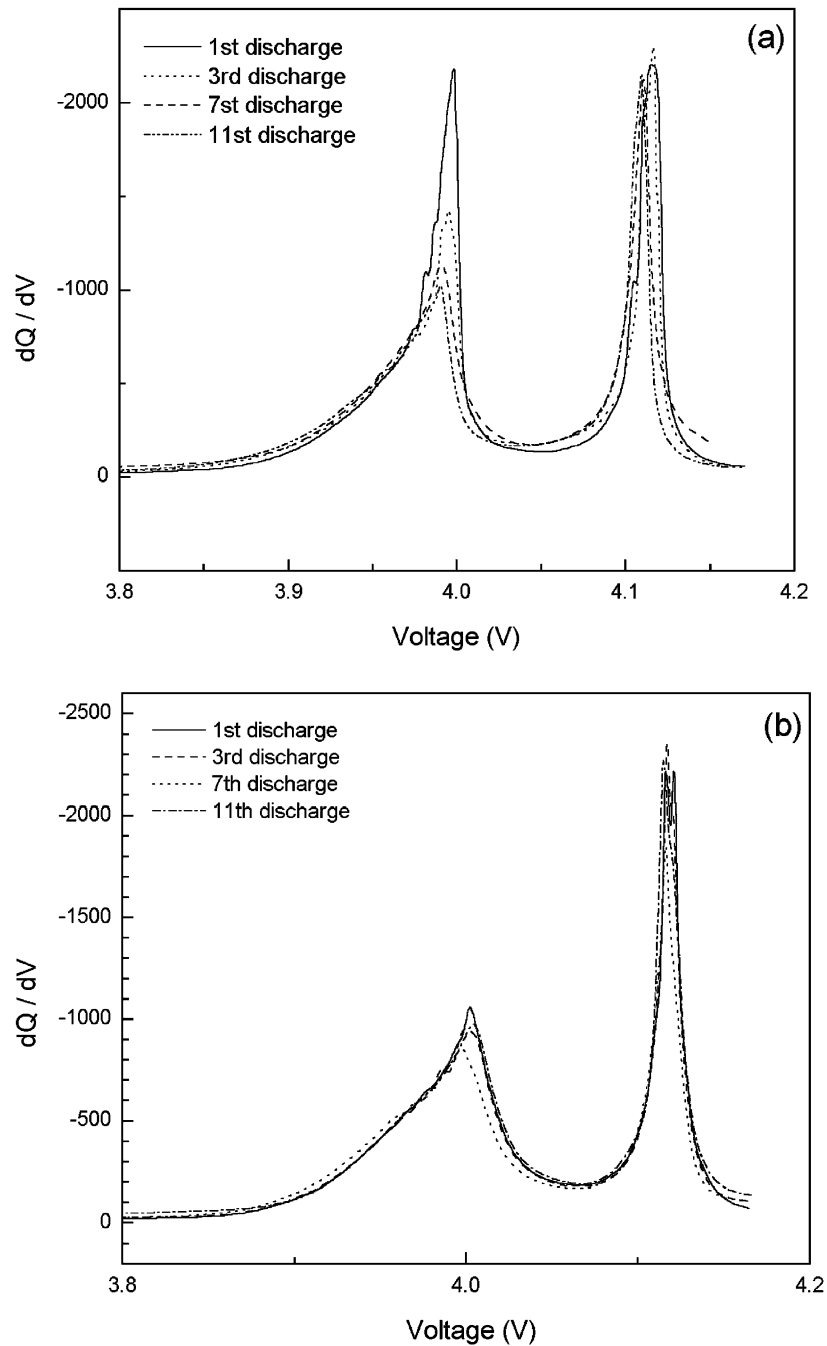


Fig. 4. Differential plot of (a) LiMn_2O_4 and (b) $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ (HTCCo) synthesized by combustion and further heat-treated at 800°C for 12 h.

4. Conclusions

By using combustion synthesis at about 280°C for 1 min and further heat-treatment, well-defined spinels $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ (M: Al, Co, Ni, Fe, or Y) are obtained. $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_4$ has a lower initial capacity than that of undoped LiMn_2O_4 but better cycleability. This demonstrates the feasibility of the combustion synthesis for preparing spinel lithium manganese oxide as cathode materials for lithium secondary batteries.

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