

리튬 이차전지용 $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$, $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ 의 합성과 그들의 혼합물의 전기화학적 특성

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Syntheses of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ and $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ and Electrochemical Properties of their Mixtures for Lithium Secondary Battery

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ABSTRACT

$\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ 와 $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ 를 단순화한 연소법에 의하여 합성하고, 그것들의 전기화학적 특성을 조사하였다. 또한 30분동안 밀링하여 준비한 $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x$ wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ ($x=9, 23, 33, 41$ and 47) 혼합물 전극의 전기화학적 특성을 조사하였다. $x=33$ 조성의 전극이 가장 큰 초기방전용량(132.0mAh/g at 0.1C)을 나타내었다. $x=9$ 조성의 전극은 비교적 큰 초기방전용량(109.9mAh/g at 0.1C)과 우수한 사이클 특성을 나타내었다. 사이클링에 따른 혼합물 전극의 방전용량의 감소는 주로 $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ 의 퇴화에 기인한다고 생각된다. 그런데 $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ 의 퇴화는 $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ 로부터 용해된 Mn이 $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ 를 둘러쌈(coating)으로써 야기되는 것으로 생각된다.

주요기술용어 : a simplified combustion method (단순화한 연소법), mixture electrodes $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x$ wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ ($\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x$ wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ 혼합물 전극), first discharge capacity (초기방전용량)

1. Introduction

Transition metal oxides such as LiMn_2O_4 ¹⁻³⁾,

LiCoO_2 ⁴⁻⁶⁾, and LiNiO_2 ⁷⁻¹⁰⁾ have been investigated in order to apply them as positive electrode (cathode) materials for lithium secondary batteries. LiMn_2O_4 is very cheap and does not bring about

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environmental pollution, but its cycle performance is not good. LiCoO_2 has large diffusivity and high operating voltage, and can be easily prepared. It has a disadvantage, however, in that it contains an expensive element, namely, cobalt. LiNiO_2 is a very promising cathode material since it has a large discharge capacity¹¹⁾ and is relatively excellent in terms of economics and environmental pollution. On the other hand, its preparation is very difficult compared with that for LiCoO_2 and LiMn_2O_4 . In order to overcome the drawbacks of LiNiO_2 and LiCoO_2 , solid solutions $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ have been studied.

The previous works studied the electrochemical properties of each of these transition metal oxides, but there is no research on the electrochemical properties of the mixtures of these transition metal oxides. LiMn_2O_4 and LiNiO_2 intercalate and deintercalate Li ions under similar conditions.

In our previous work, we showed that the electrochemical properties of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ prepared by a simplified combustion method were good¹²⁾. In this work, $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ and $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ are synthesized by a simplified combustion method in which the preheating step is omitted, and their electrochemical properties are investigated. In addition, electrodes of mixtures of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ and $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, having the best electrochemical properties among $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$, are also prepared and their electrochemical properties are examined.

2. Experimental

Starting materials for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ were LiNO_3 , $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_2CONH_2 (urea) with purities 98%. The starting materials in wanted compositions was mixed homogeneously by a magnetic stirrer. The mixed sample was in light reddish brown color. This mixed sample was calcined twice at 750°C for 24h in air in 0.6 mole ratio of urea to nitrate by heating in a rate of $100^\circ\text{C}/\text{h}$ and by cooling in a rate of $100^\circ\text{C}/\text{h}$.

Starting materials for $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ were LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_2CONH_2 (urea) with purities 98%. The starting materials in wanted compositions were mixed homogeneously by a magnetic stirrer. The mixed samples were in light reddish green color. These mixed samples were calcined at $750\text{--}900^\circ\text{C}$ for 3–24h in air in different mole ratios of urea to nitrate (0.6–4.8). Mixtures with the compositions $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x$ wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ ($x=9, 23, 33, 41$ and 47) were prepared by using SPEX mill. The volume of vial was 20ml and ZrO_2 balls ($\phi = 3\text{mm}$) were used. The phase identification of the prepared samples was carried out by X-ray diffraction (XRD, Rigaku III/A type) analysis using $\text{CuK}\alpha$ radiation. The morphologies of the samples were observed using a scanning electron microscope (SEM) and a field emission scanning electron microscope (FE-SEM). The surface of mixture electrodes was also analyzed by electron probe microanalysis (EPMA). To measure the electrochemical properties, the electrochemical cells consisted of the prepared sample as a positive electrode, Li metal as a negative electrode, and an electrolyte of 1M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). A Whatman glass was used as a

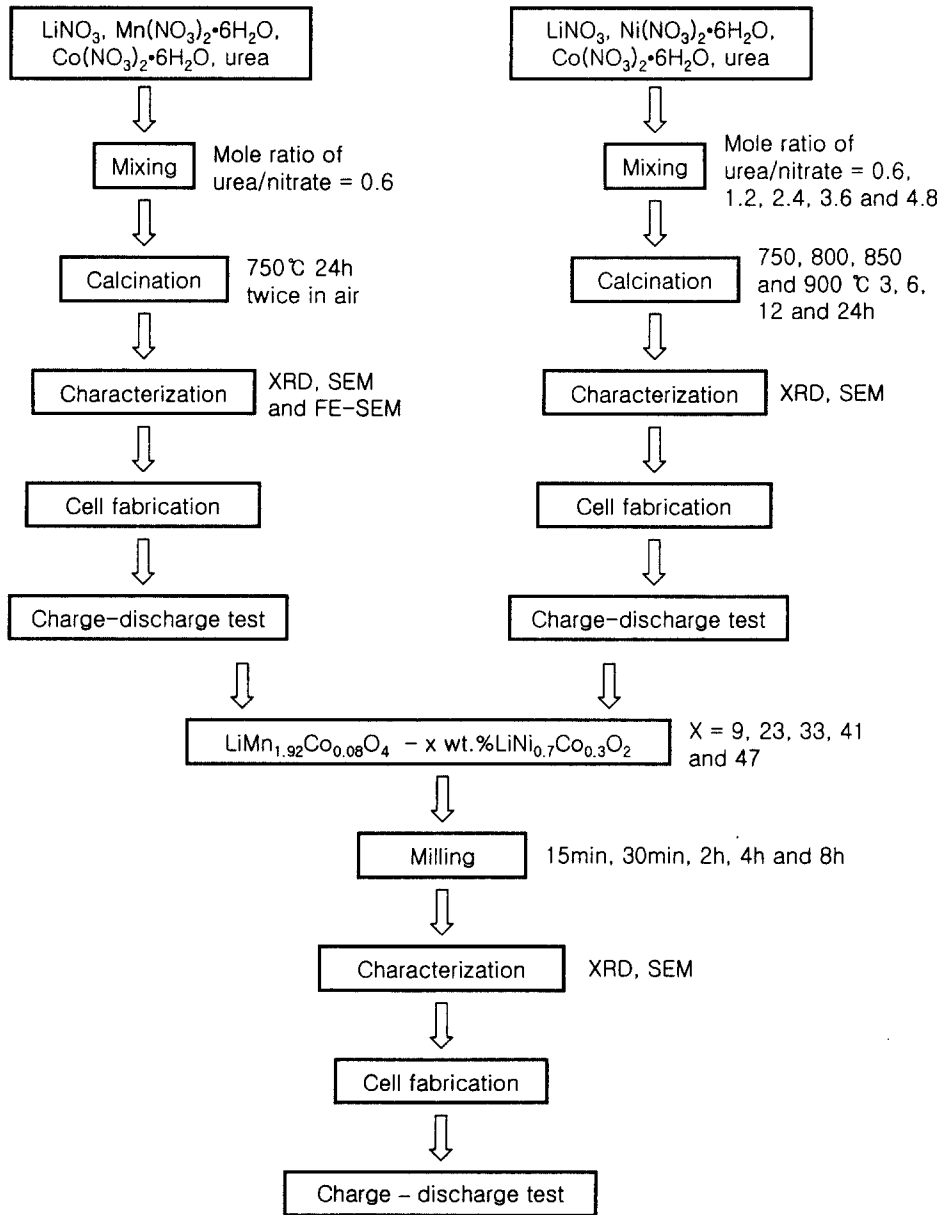


Fig. 1. Experimental procedure for the $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$, $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ and $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ electrodes.

separator. The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, active material, acetylene black and polyvinylidene fluoride (PVDF) binder with N-methyl-2-pyrrolidone (NMP) were mixed in a weight ratio 85:10:5 on Al foil. By introducing the Li metal, the Whatman glass-fiber, the positive electrode and the electrolyte, the cell was assembled. All the electrochemical tests were performed at room temperature with a battery charge-discharge cycle tester at 0.1 and 0.5C in a potential range from 3.0 to 4.4V. Fig. 1 summarizes the experimental procedure.

3. Results and Discussion

Fig. 2 shows XRD patterns of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ synthesized with a simplified combustion method by calcining at 750°C for 24h and 48h. The sample calcined for 24h contained a small amount of Mn_2O_3 and a phase with spinel structure. The sample calcined for 48h has only the phase with spinel structure.

Fig. 3 shows SEM and FE-SEM photographs of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ synthesized with a simplified

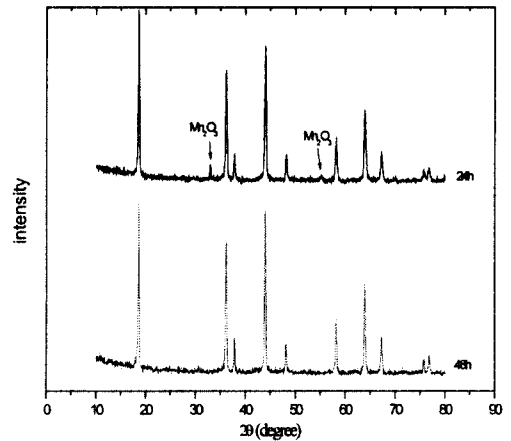


Fig. 2. XRD patterns of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ synthesized by a simplified combustion method for different calcination times

48h. SEM photograph shows that the smaller spherical particles with sizes $100\sim 200\text{nm}$ cluster around the larger spherical particles with sizes $1\sim 2\mu\text{m}$. FE-SEM photograph shows that the larger particles ($1\sim 2\mu\text{m}$) form by clustering of the same variations of discharge capacity at 0.1A particles ($100\sim 200\text{nm}$).

Fig. 4 shows tC with the number of cycles n for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ synthesized with a

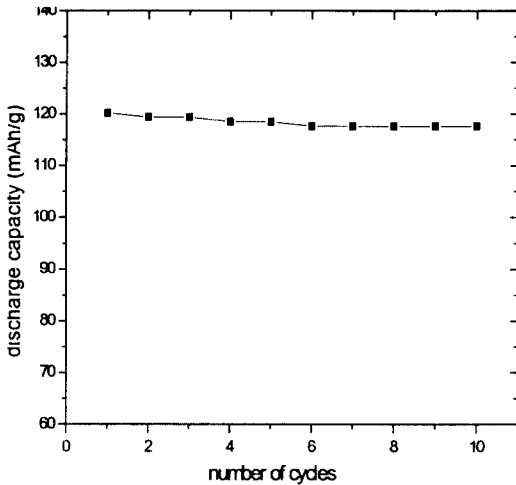


Fig. 4 Variation of discharge capacity with the number of cycles for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ synthesized with a simplified combustion method by calcining at 750°C for 48h

750°C for 48h. $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ has a relatively large first discharge capacity at 0.1C of 120.3mAh/g and the discharge capacities at 6~10th cycle are all 117.6mAh/g, indicating an excellent cycling performance.

In order to find the optimum conditions for synthesis, $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ is synthesized by varying the mole ratio of urea to nitrate (0.6, 1.2, 3.6, 4.8 and 9.6), synthesizing time (3, 6, 12 and 24h) and synthesizing temperature (750 , 800 , 850 and 900°C).

From the results of XRD (R-factor and intensity ratio I003/I104) and SEM, the optimum condition for synthesizing $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ by a simplified combustion method, is the calcinations at 800°C for 12h in air in 3.6 mole ratio of urea to nitrate.

Fig. 5 gives the XRD patterns for $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y=0.1, 0.3$ and 0.5) synthesized by a simplified combustion method at 800°C for 12h in air in 3.6 mole ratio of urea/nitrate. All the

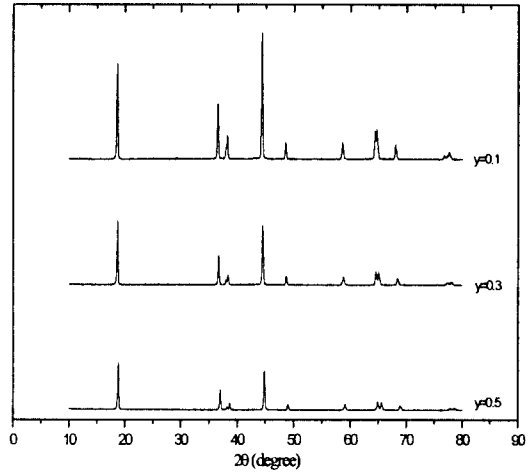


Fig. 5. XRD patterns for $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y=0.1, 0.3$ and 0.5) synthesized by a simplified combustion method at 800°C for 12h.

samples revealed the formation of the phase with $R\bar{3}m$ structure. The intensities of the peaks decrease as the value of y increases.

Fig. 6 gives the SEM photographs of the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y=0.1, 0.3$ and 0.5) synthesized at 800°C for 12h in 3.6 mole ratio of urea/nitrate. The particle size decreases as the value of y increases. The particles with $y=0.3$ are in the shape of sphere with the most homogeneous particle size.

Fig. 7 shows the variations of discharge capacities at 0.5C and 0.1C with the number of cycles for the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y=0.1, 0.3$ and 0.5) synthesized by a simplified combustion method at 800°C for 12h in air in 3.6 mole ratio of urea/nitrate. The first discharge capacities at 0.5C are 84.5 ($y=0.1$), 156.2 ($y=0.3$) and 134.5 ($y=0.5$) mAh/g. The sample with $y=0.3$ has the largest first discharge capacity and relatively good cycling performance. The sample with $y=0.3$ shows the first discharge capacity at 0.1C of 181mAh/g, but its cycling performance is

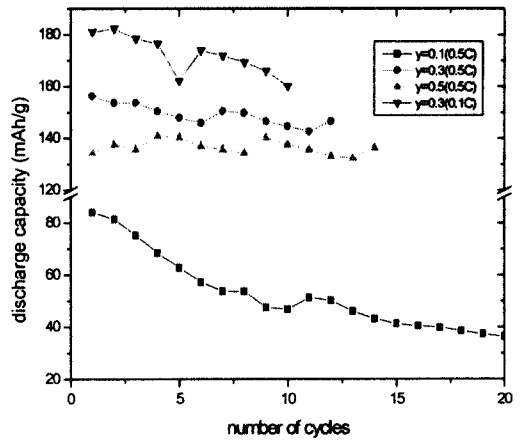


Fig. 7. Variations of discharge capacities with the number of cycles for $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y=0.1, 0.3$ and 0.5) synthesized by a simplified combustion method.

$\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ phase becomes stronger.

Fig. 9 show s SEM photographs for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ ($x=9, 23, 33, 41$ and 47) after milling for 30min. In the mixture with $x=9$ the particles were strongly clustered. In the mixtures with $x=23, 41$ and 47 the particles were less clustered than in the

worse than that at 0.5C.

Fig. 8 shows XRD patterns of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ ($x=9, 23, 33, 41$ and 47) after milling for 30min. As the value of x increases, the peak of $R\bar{3}m$ structure for

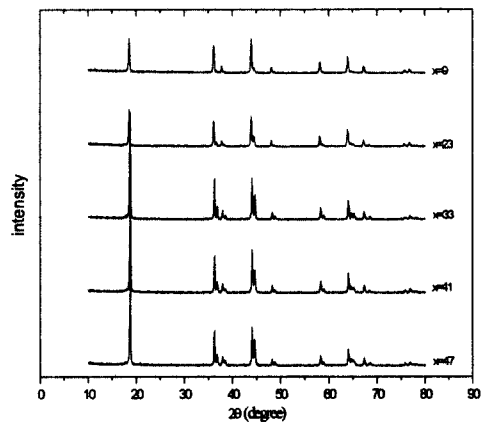


Fig. 8. XRD patterns of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ ($x=9, 23, 33, 41$ and 47) synthesized by a simplified combustion method after milling for 30min.

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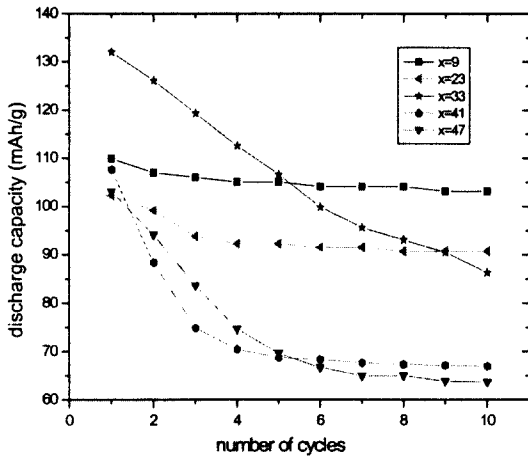


Fig. 10 Variations of discharge capacities at 0.1C with the number of cycles for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ - x wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ (x=9, 23, 33, 41 and 47) synthesized by a simplified combustion method after milling for 30min.

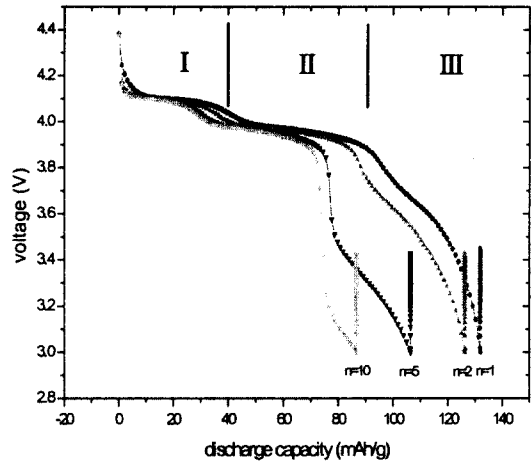


Fig. 11. Variations of voltage vs. discharge capacity curves at 0.1C with the number of cycles for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ -33 wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ synthesized by a simplified combustion method after milling for 30min.

the lower plateau (region II) and of the region III remain nearly constant. At the fifth cycle, the lengths of the higher plateau (region I) and the lower plateau (region II) decrease a little and the length of the region III decreases in a quite large amount. At the tenth cycle, the lengths of the higher and the lower plateau (I and II regions) remain almost constant, but the length of the region III decrease in a large amount. $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ is known to have two voltage plateau in the charge-discharge voltage range of 3.5~4.3V and $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ is known not to have clear voltage plateau in the charge-discharge voltage range of 2.8~4.3V. In the voltage vs. discharge capacity curve of $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.08$), the voltage decreases very rapidly under about 3.7V because intercalation a very small amount of Li^+ contributes to the discharge capacity. The above result shows that the discharge capacity decreases mainly under about 3.8V. Therefore,

it is considered that the discharge capacity fading results mainly from the degradation of $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$.

The discharge capacities of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ in the mixtures with x=9, 23, 33, 41 and 47 are calculated to be 109.1, 92.3, 80.0, 70.6 and 63.2mAh/g on the basis of the discharge capacity of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ of about 120mAh/g at 0.1C. Fig. 9 shows that the discharge capacities at 0.1C of the mixtures with x=9, 23, 33, 41 and 47 at the 10th cycle are 103.2, 90.7, 86.3, 67.0 and 63.7mAh/g, respectively. These values of discharge capacities are very similar to the calculated values of the discharge capacities of $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ in the mixtures.

Fig. 11 shows the length of the region III, which is related to the discharge capacity of $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, decreases rapidly as the number of cycles increases. These two points shows that $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ contributes mainly to the discharge capacities of the mixtures and large

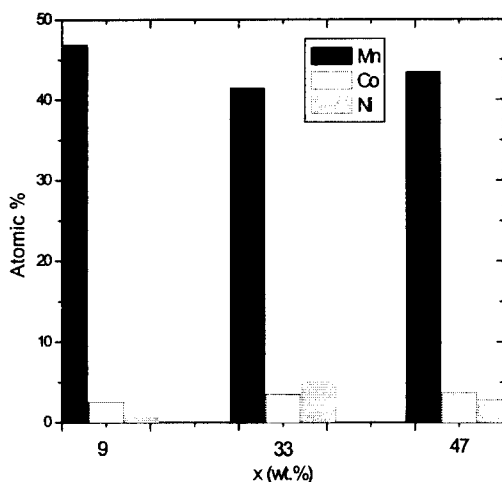


Fig. 12. EPMA results of the electrode surfaces of the $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ mixtures after 10 charge-discharge cycles at 0.1C.

part of $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ is degraded.

Fig. 12 shows the EPMA results of the electrode surfaces of the $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ mixtures after 10 charge-discharge cycles at 0.1C. The atomic percentage of Ni does not increase proportionally as the value of x increases. The atomic percentage of Mn is high and remains almost constant.

It is considered that, $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ is coated with Mn and the quantity of the coated Mn increases as the number of cycles increases. The increase in the atomic percentage of Ni is not proportional to the value of x (Fig. 12). The coated Mn is considered to prevent Li ions from intercalation into $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ or from deintercalation from $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$.

Fig. 13 shows the variations of discharge capacity at 0.5C with the number of cycles n for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ (x=9,

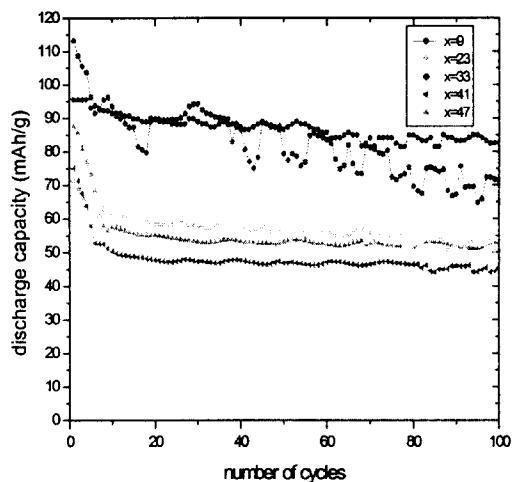


Fig. 13. Variations of discharge capacities with the number of cycles at 0.5C for $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4 - x \text{ wt.}\% \text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ (x=9, 23, 33, 41 and 47) synthesized by a simplified combustion method after milling for 30min.

23, 33, 41 and 47) after milling for 30min. The first discharge capacities of the mixtures with x=9, 23, 33, 41 and 47 are 95.6, 71.4, 113.3, 75.1 and 87.5mAh/g, respectively. The mixtures with 23, 33, 41 and 47 show rapid decreases in the discharge capacity between n=1 and n=11, and then the discharge capacities remain nearly constant from n=12. The mixture with x=9 has smaller first discharge capacity than the mixture with x=33, but it shows the best cycling performance.

4. Conclusions

$\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ synthesized by a simplified combustion method by calcining at 750°C for 48h has relatively large discharge capacity (120.3 mAh/g at 0.1C) and excellent cycling performance. $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ (y=0.1, 0.3 and 0.5) were synthesized by mixing in the mole ratio of urea/nitrate 3.6 and calcining at 800°C for 12h which are optimum conditions for synthesis.

$\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ had the largest first discharge capacity 156.2mAh/g at 0.5C and the best cycling performance.

Mixtures $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$ - x wt.% $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ (x=9, 23, 33, 41 and 47) are prepared by milling for 30min and their electrochemical properties are investigated. The electrode with x=33 had the largest discharge capacity (132.0mAh/g). The electrode with x=9 had a relatively large first discharge capacity (109.9mAh/g at 0.1C) and good cycling performance. The decrease in the discharge capacity of the mixture electrodes with cycling is considered to result mainly from the degradation of $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, caused probably by coating of $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ with Mn dissolved from $\text{LiMn}_{1.92}\text{Co}_{0.08}\text{O}_4$.

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