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Characteristics of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Powder Prepared by Different Method in Lithium Rechargeable Batteries

Sung-Keun Kim[1], *Woon-Tae Jeong*[2], *Hong-Ki Lee3*, *Joongpyo Shim*[1,*]

[1] Department of Chemical Engineering, Kunsan National University, Jeonbuk, 573-701, Korea
[2] Umicore Korea Ltd, Chungnam, 330-200, Korea
[3] Fuel Cell Regional Innovation Center, Woosuk University, Jeonbuk, 565-701, Korea
[*]E-mail: jpshim@kunsan.ac.kr

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$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials were synthesized by different synthetic routes; through spray-drying, combustion, or solid-state reactions. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), particle size analysis, and charge/discharge cycling. All the prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were identified as hexagonal structures and exhibited discharge capacities of ca. 130-140 mAh/g at 2.8-4.3 V. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder prepared through the spray-drying method showed better electrochemical properties, such as discharge capacity, rate capability, and constant cycling, over those synthesized from combustion and solid-state reaction.

Keywords: Lithium-ion batteries, spray-drying, cathode, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, combustion

1. INTRODUCTION

Rechargeable lithium-ion batteries have been developed and $LiCoO_2$ has been widely used as cathode material because of its high cycleability. [1] However, its capacity is limited due to a structural change above 4.3V and cobalt is relatively expensive and toxic compared to nickel, manganese and iron which can form various layered oxides with lithium. Many researchers have tried to develop low cost and less toxic materials such as nickel ($LiNiO_2$), manganese ($LiMn_2O_4$ or $LiMnO_2$) and iron ($LiFePO_4$)-based materials.

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ compounds have thus been studied as the most promising cathode material for lithium-ion batteries due to their good cycleability, no structural transformation during cycling, and relatively low cost compared to layered oxides such as $LiCoO_2$. [2] $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been prepared by a solid-state reaction which has several disadvantages, such as inhomogeneous composition, irregular morphology, large particle size, and long heating times followed by several grinding and annealing processes. [3] In this work, we report on the synthesis and electrochemical characteristics of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials prepared from three different methods; spray-drying, combustion and solid-state reaction.

2. EXPERIMENTAL PART

For the spray-drying (SD) method, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ precursors were prepared using $LiCH_3COO\cdot 2H_2O$, $Ni(CH_3COO)_2\cdot 4H_2O$, $Co(CH_3COO)_2\cdot 4H_2O$, $Mn(CH_3COO)_2\cdot 4H_2O$ with a molar ratio of Li/Me = 1.1 (Me=Ni, Co and Mn). These metal acetates were dissolved in deionized water. The resulting solution was sprayed to form a homogeneous mixture of precursors at 150^{o}C. The mixed precursor powder was heated to 400^{o}C for 4 h in air. Then the obtained powder was ground in a mortar and re-annealed at 900^{o}C for 15 h in air. [4]

For the combustion method (CB), $Li(NO_3)_2\cdot 4H_2O$, $Ni(CH_3COO)_2\cdot 4H_2O$, $Co(CH_3COO)_2\cdot 4H_2O$, and $Mn(CH_3COO)_2\cdot 4H_2O$ were dissolved in deionized water with a molar ratio of Li/Me = 1.1 (Me=Ni, Co and Mn). The dissolved solution was heated at 80-90^{o}C to make a green-colored gel. It was then burned and transformed into a black sponge-like fluffy material. The powder was additionally sintered at 900^{o}C for 15 h.

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials were prepared by the solid-state reaction (SS) of precursors. The precursors were prepared in the same manner as in the spray-drying method above. The metal acetate precursors were well-mixed in a mortar and pressed into pellet. The pellet was preheated at 400^{o}C in air for 4 h and then sintered at 900^{o}C for 15 h.

The thermo gravimetric analysis (TGA) for the mixture of precursors was conducted in air atmosphere to observe the temperature for precursor decomposition and calcination. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (Bruker M18XCE) with Cu-Kα radiation. The particle morphology and size distribution were observed by scanning electron microscopy (SEM) and a particle size analyzer (Analysette 22, Fritsch).

Cathodes were made by coating a mixture of 88% of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, 6% carbon black, and 6% polyvinylidene fluoride (PVdF) binder onto aluminum foil. The electrode was dried under vacuum at 120℃ for 12 h and then pressed. The loading amount of active material was 8-10 mg/cm^2. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in a 1:1 volume ratio. The Swagelok-type cell was assembled in an Ar-filled glove box and tested at room temperature. Positive and negative electrodes were separated by a polypropylene membrane (Celgard 2400). A metallic lithium foil was used as the counter electrode. This cell was discharged until 2.8V and charged up to 4.3 ~ 4.7V by battery cycler (WonA Tech, WBCS 3000).

3. RESULTS AND DISCUSSION

The temperature for the decomposition of precursors, metal acetates containing lithium, nickel, manganese and cobalt, was observed using by thermo-gravimetric analysis (TGA), as shown in Fig. 1. Most of hydrate in precursor was vaporized around 130°C and then, the decomposition of acetate started around 300°C and finished before 500°C. Therefore, we decided that the temperature and time for preheating was 400°C and 4hours to decompose the acetate fully and then form the layered oxide.

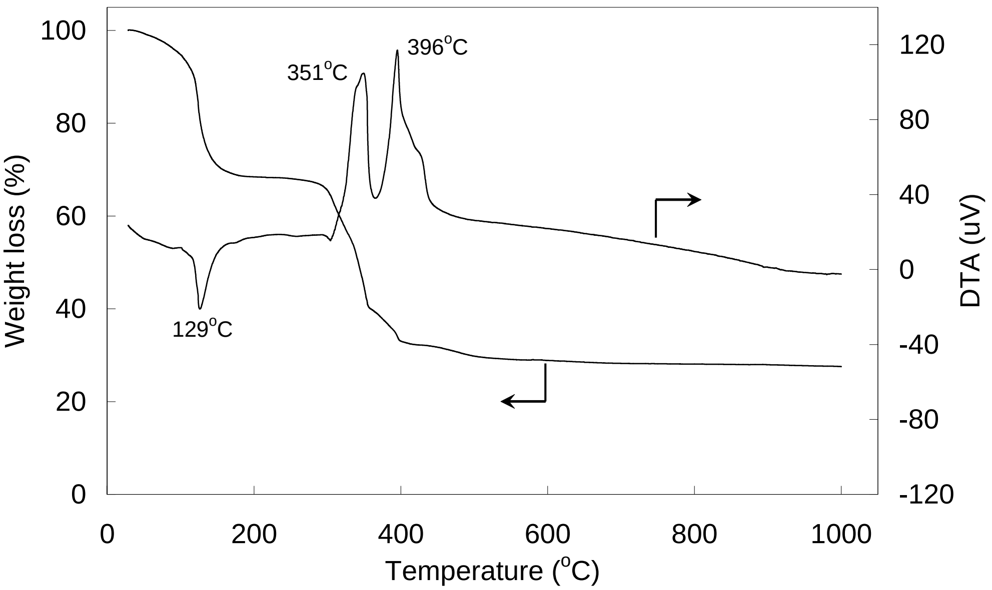

Figure 1. TGA of the mixture of precursors in air.

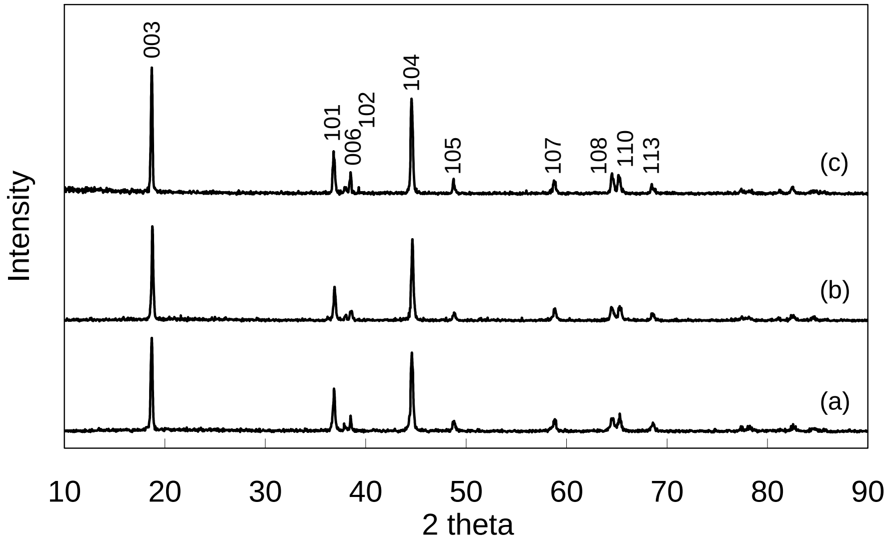

Figure 2. X-ray diffraction patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ compounds prepared by (a) spray-drying method, (b) combustion method, and (c) solid-state reaction.

The powder XRD patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ compounds prepared from different synthetic methods are shown in Fig. 2. All the prepared materials could be identified as α-$NaFeO_2$ structures with a space group of $R\bar{3}m$. This was determined by the fact that all of the XRD patterns accorded well with a typical hexagonal pattern and showed a clear split between (108) and (110) peaks. [6] Table 1 shows the lattice parameters and the unit cell volume calculated from the XRD results. The lattice parameters, a = 2.8602Å and c = 14.2239Å, and the unit cell volume, V = 100.77Å^3, of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder (SD) are very consistent with the values reported by Ohzuku.[1,7] Other materials (CB and SD) show a slightly lower value.

Table 1. Lattice parameter, mean particle size of the materials prepared from different method.

Method	a(Å)	c(Å)	c/a	V(Å^3)	Mean particle size (μm)
SD	2.8602	14.2239	4.97	100.77	0.95
CB	2.8532	14.2210	4.98	100.26	1.03
SS	2.8560	14.2204	4.98	100.45	1.14
Sample[a]	2.862	14.227	4.97	100.91	NA

[a] N. Yabuuchi, T. Ohzuku, *J. Power Sources*, 119-121 (2003) 171

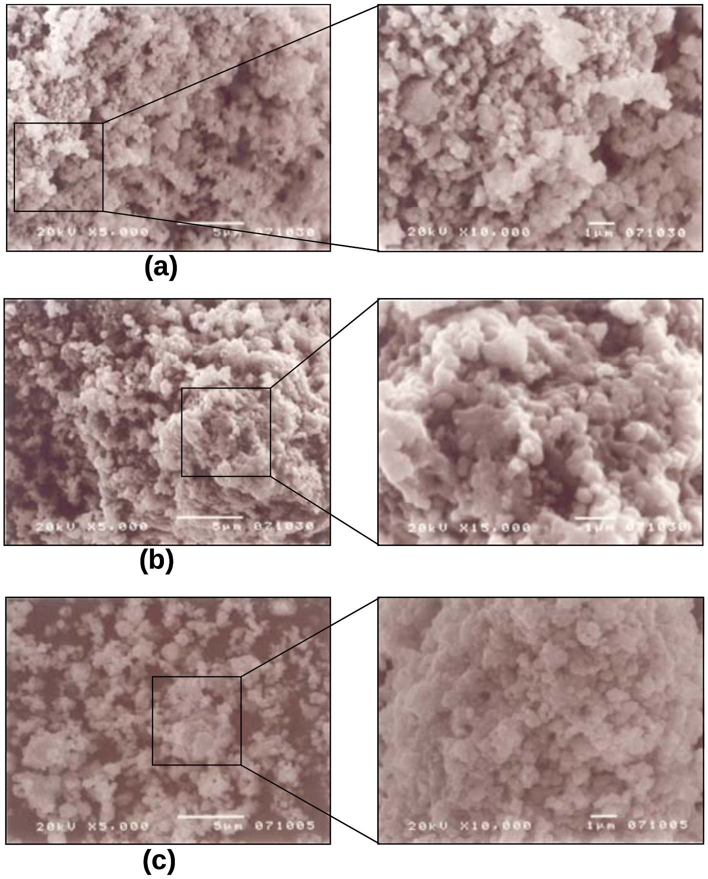

Figure 3. SEM images of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders prepared by (a) spray-drying method, (b) combustion, (c) solid-state reaction

Fig. 3 shows SEM images of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders. Although the particle morphology is not clearly shown, all the images show the large agglomeration of small particle with a size of ~1 μm. The particle size distribution in Fig. 4 shows that two of the powders (SD and CB) have a more uniform size distribution in the range of 0.2 to 3 μm than that with a broad distribution (SS) from 0.2 to 10 μm . However, Table 1 shows very similar mean particle size for all three materials.

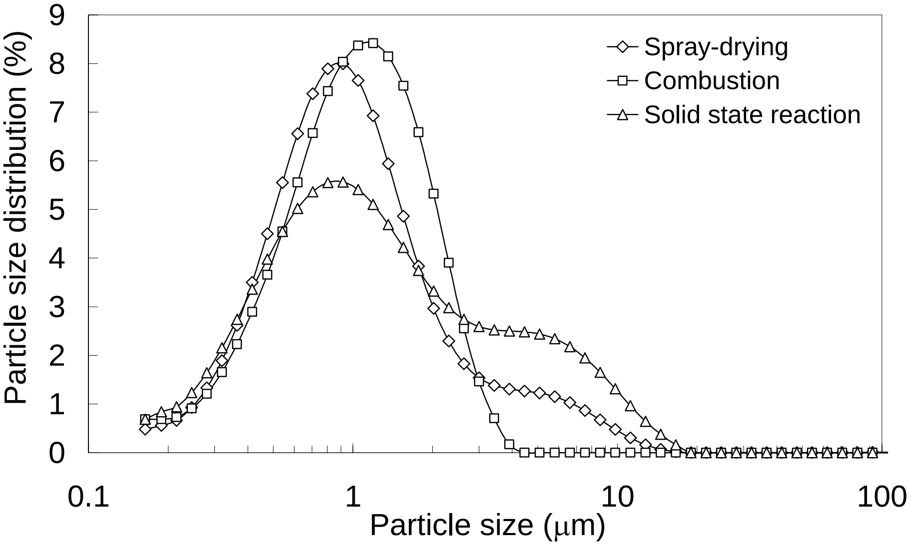

Figure 4. Particle size distribution of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders

Fig. 5 shows the initial charge and discharge curves of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes at 6.0 mA/g in the range from 2.8 to 4.3 V at 25°C. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes (SD, CB and SS) show the initial charge/discharge capacities of 171/139 (~81% of coulombic efficiency), 170/128 (~75% of coulombic efficiency) and 174/134 mAh/g (~79% of coulombic efficiency), respectively. All of the materials were prepared from different methods shown by a very similar initial capacity. However, the irreversible capacity observed in the first cycle was about 30-40 mAh/g which is slightly higher than that reported by Ohzuku.[1] The dQ/dV plots of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes in Fig. 5 (d) show one redox peak at 3.6-3.8V. Ohzuku's group and Chang's group proposed that the Ni^{2+}/Ni^{4+} couple occurs at 3.7-4.0V and the oxidation of Co^{3+} to Co^{4+} follows above 4.5V.[8, 9]

As shown in Fig. 6, the rate capability tests were carried out to examine the lithium-ion transfer in the solid state. The cell was charged at 0.2 C (1 C = 160 mAh/g)[7] until it was at 4.3 V and then discharged to 2.8 V at different C rates from 0.2 C to 5 C. Fig. 6 (a) shows the discharge curves of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (SD) with different C rates. The discharge capacity rapidly decreases with increasing C rate and those are 73 and 16 mAh/g at 2 and 5 C which are assigned to 51% and 11% capacity retention for the initial capacity, respectively. As shown in Fig. 6, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (SD) exhibits better rate capability than the other two powders (CB and SS). Poor rate capability of this material compared to the results reported in literature might be due to less crystallinity of the powder, low carbon content in the electrode, or a lack of skill in electrode preparation. The skill to make uniform electrodes should be improved for further study. Fig. 7 shows specific capacity as a function of cycle number for a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell cycled through various voltage ranges at 0.2 C (32 mA/g) and 25°C. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cells showed very similar cycleability up to 4.5V of charging voltage. From 4.6V, the electrode (SS) showed faster capacity fading rather than those (SD and CB). The discharge capacity (SD) showed slightly higher than that (CB).

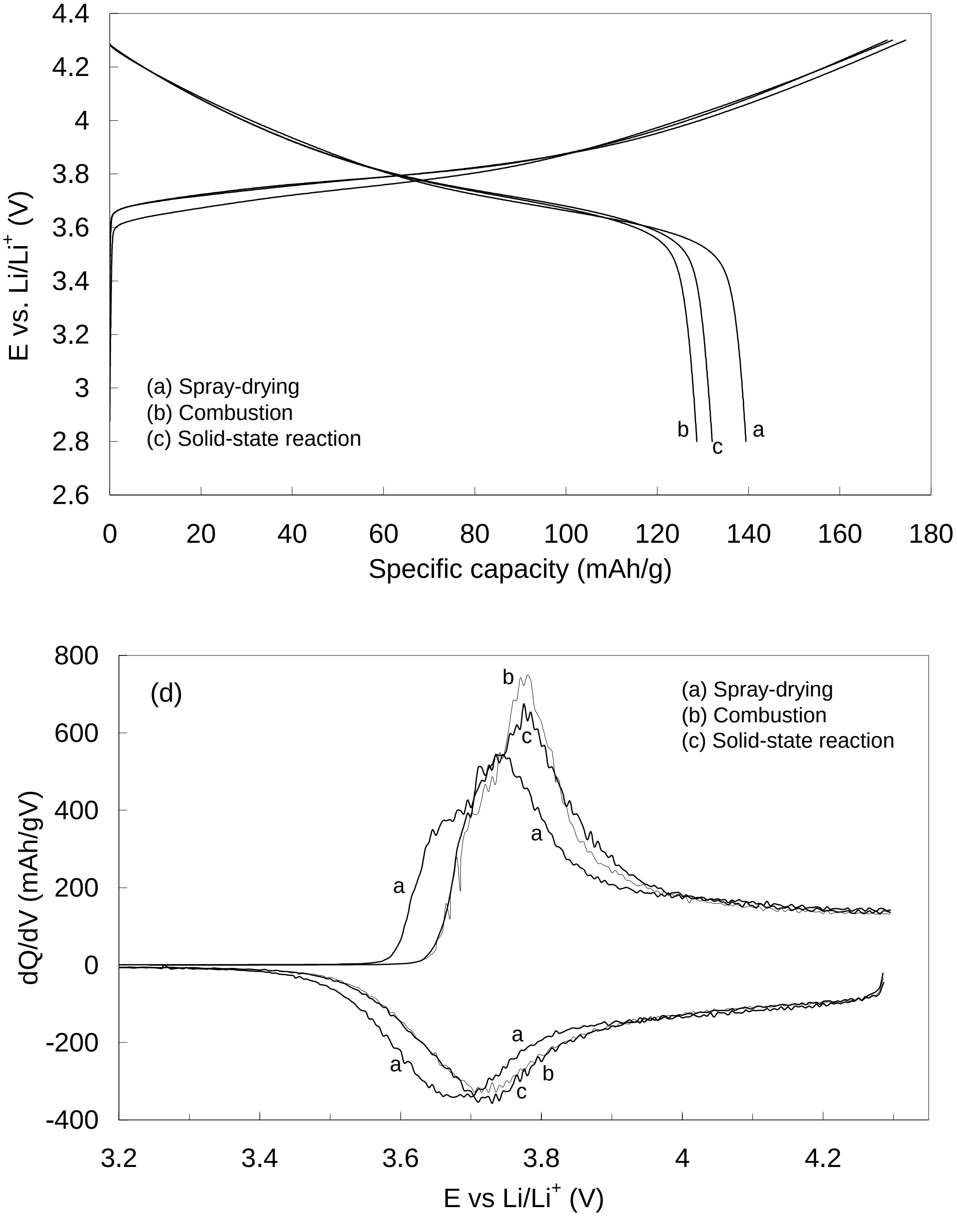

Figure 5. Initial charge/discharge curves of differential $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes prepared by (a) spray-drying method, (b) combustion method, and (c) solid-state reaction. (d) dQ/dV plot

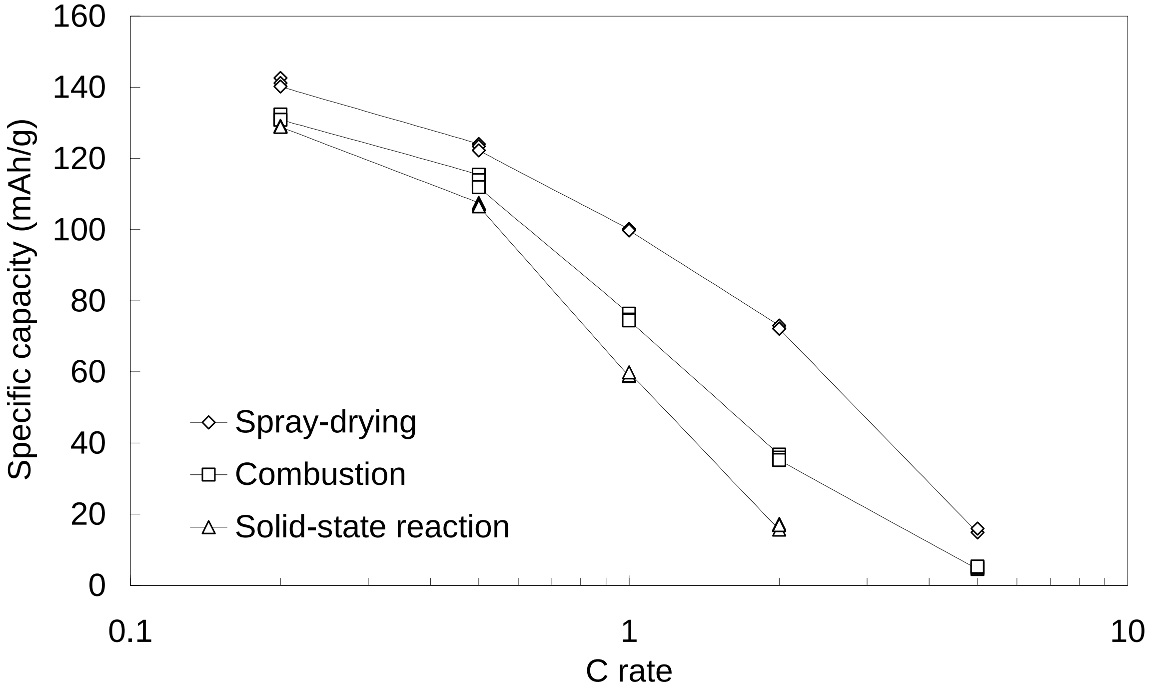

Figure 6. Discharge capacity curves at different discharge rates at C/5, C/2, 1C, 2C, 5C for the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes ranging from 2.8 to 4.3 V.

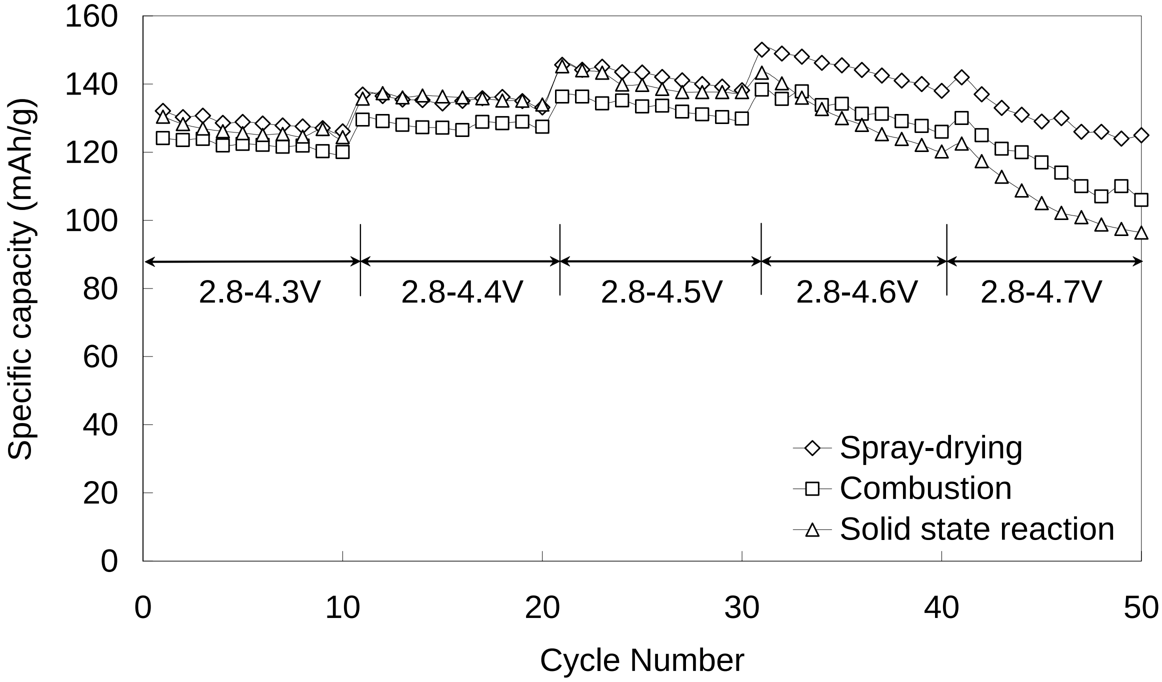

Figure 7. Discharge capacities as a function of cycle number in various voltage ranges at 0.2C.

4. CONCLUSIONS

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials were synthesized from three different methods; spray-drying, combustion, and solid-state reaction. The results from XRD showed that the crystal structure of all the powders was hexagonal structure and the unit cell volume was different according to the synthetic method used. The SEM and particle size analysis of the prepared materials showed uniform size distribution around ~1 µm. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes delivered a discharge capacity of ca. 130-140 mAh/g between 2.8 and 4.6 V and showed good cycleability until the charge voltage reached to 4.6 V. It was found that the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material prepared through the spray-drying method showed the largest unit cell volume and better cycleability over those obtained from the combustion and solid-state reaction methods.

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