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Microwave Synthesis of Spherical $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ Powders as a Positive Electrode Material for Lithium Batteries

Ki-Soo Lee,[†] Seung-Taek Myung,[‡] and Yang-Kook Sun*[,†]

Center for Information and Communication Material,
Department of Chemical Engineering, Hanyang University,
Seoul 133-791, South Korea, and Department of Chemical
Engineering, Iwate University, 4-3-5 Ueda, Morioka,
Iwate 020-8551, Japan

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Recently, a solid solution based on $LiNiO_2$, $LiCoO_2$, and $LiMnO_2$ as end members, $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ with α-$NaFeO_2$ structure ($R\bar{3}m$ space group), was introduced to overcome the significant drawbacks of $LiCoO_2$, $LiNiO_2$, and $LiMnO_2$.[1] Lower Co content in $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ ($x \leq 1/3$) is of particular interest because the reduced amounts of Co and Ni in the crystal structure contribute to improved thermal and safety properties.[2] Material chemistry of the $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ is also interesting; the oxidation states of Ni, Co, and Mn are 2+, 3+, and 4+, respectively.[3] Redox couples of the compound are combined with $Ni^{2+/3+/4+}$ and $Co^{3+/4+}$, corresponding to the theoretical capacity of about 280 mA h (g-oxide)$^{-1}$. When the material is charged to 4.3 V ($Li_{0.4}[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$), the average oxidation states of Ni and Co are close to 3+ and 3.5+, respectively.[3] The Mn^{4+} is electrochemically inactive in the moderate operation voltage range.[3] Such a synergetic effect, that is, relatively lower oxidation state compared to $Li_{0.4}CoO_2$ (average oxidation state of Co: 3.6+) and $Li_{0.4}NiO_2$ (average oxidation state of Ni: 3.6+) at 4.3 V and the presence of tetravalent Mn in the host structure provides a significant structural stability during repetitive Li^+ de-/intercalation.

There are a few comparative studies for $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ ($x \leq 1/3$).[4] Sun et al. and Whittingham et al. reported that the specific discharge capacity was the highest when $x = 0.2$ in $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$. Though a relatively smaller amount of Co was contained in the composition, it shows electric conductivity and rate capability similar to that of $x = 1/3$ in $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$.[4] In thermal stability, $x = 0.2$ in $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ also exhibits an improved property compared to that of $x = 1/3$ in $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$.[4] Therefore, it is thought that using $x = 0.2$ in $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ composition would be more beneficial in respect to specific capacity, electronic conductivity, rate capability, thermal property, and so on.

In fact, a large amount of Ni containing compounds, i.e., $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{0.5}O_2$, etc., usually show impurities such as NiO, $LiNiO_x$, and Li_2MnO_3 because of the difficulty of phase formation between Ni and Mn when a conventional solid-state reaction used.[5] For this reason, many research groups employed metal hydroxides as precursors to produce homogeneous layered $LiMO_2$ (M = Ni, Co, Mn). Even though they prepared the material, dehydration and prolonged calcination of the precursor at higher temperature are necessary to produce high-purity $Li[(Ni_{1/2}Mn_{1/2})_{1-x}Co_x]O_2$ ($x \leq 1/3$).[4,5]

However, such demerits can be readily solved by using microwave irradiation. Many researchers use the microwave to synthesize ceramic materials.[6] Microwave synthesis is generally quite faster, simpler, and very energy efficient. The exact nature of microwave interaction with reactants during the synthesis of materials is somewhat unclear and speculative. Several efforts using microwave were also made for synthesis of electrode materials such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$.[7] Though the targeted phase formation was successful, their electrochemical properties were not so satisfactory because of their lower crystallinity. Because of the poor crystallization even after microwave treatment, most of materials were calcined again at higher temperature for a long time to improve their crystallinity.[7] In this study, therefore, we would like to introduce a one-step synthesis of highly crystalline $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ using microwaves irradiation.

To prepare $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ powders, we first synthesized spherical $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$ via coprecipitation as shown in Figure 1a. It is observed that XRD pattern of the as-prepared $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$ is consistent of the typical fingerprint of $M(OH)_2$ (M = Ni, Co, Mn) structure.[5] No other peak is observed in the XRD pattern, which means that homogeneous hydroxide was formed by coprecipitation. Spherical secondary particles seem to be closely piled (needle shape grains) acicular primary particles in the SEM image. A pellet of $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$ hydroxide and $LiOH\cdot H_2O$

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* Corresponding author. Tel: 82-2-2220-0524. Fax: 82-2-2282-7329. E-mail: yksun@hanyang.ac.kr.
[†] Hanyang University.
[‡] Iwate University.

(1) Ohzuku, T.; Makimura, Y. *Chem. Lett.* **2001**, *30*, 744. Ammundsen, B.; Paulsen, J. *Adv. Mater.* **2001**, *13*, 943. Lu, Z.; MacNeil, D. D.; Dahn, J. R. *Electrochem. Solid-State Lett.* **2001**, *4*, A200.

(2) Kang, S.-H.; Amine, K. *J. Power Sources* **2003**, *119−121*, 150. Myung, S.-T.; Komaba, S.; Kurihara, K.; Hosoya, K.; Kumagai, N.; Sun, Y.-K.; Izumi, N.; Yonemura, M.; Kamiyama, T. *Chem. Mater.* **2006**, *18*, 1658.

(3) Ueda, A.; Aoyama, S. *Proceedings of the 42nd Battery Symposium in Japan*, Yokohama, Japan, 2001; pp 130−131. Yoon, W.-S.; Balasubranian, M.; Chung, K. Y.; Yang, X.-Q.; McBreen, J.; Grey, C. P.; Fischer, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 17479.

(4) Oh, S. W.; Park, S. H.; Park, C.-W.; Sun, Y.-K. *Solid State Ionics* **2004**, *171*, 167. Ngala, J. K.; Chernova, N. A.; Ma, M.; Mamak, M.; Zavalij, P. Y.; Whittingham, M. S. *J. Mater. Chem.* **2004**, *14*, 214. Shizuka, K.; Kobayashi, T.; Okahara, K.; Okamoto, K.; Kanzaki, S.; Kanno, R. *J. Power Sources* **2005**, *146*, 589. Jiang, J.; Eberman, K. W.; Krause, L. J.; Dahn, J. R. *J. Electrochem. Soc.* **2005**, *152*, A566.

(5) Amine, K.; Tukamoto, H.; Yasuda, H.; Fujita, Y. *J. Electrochem. Soc.* **1996**, *143*, 1607. Myung, S.-T.; Komaba, S.; Hosoya, K.; Hirosaki, N.; Miura, Y.; Kumagai, N. *Chem. Mater.* **2005**, *17*, 2427. Myung, S.-T.; Lee, M.-H.; Komaba, S.; Kumagai, N.; Sun, Y.-K. *Electrochim. Acta* **2005**, *50*, 4800.

(6) Rao, K. J.; Vaidhyanathan, B.; Ganguli, M.; Ramakrishnan, P. A. *Chem. Mater.* **1999**, *11*, 882. Malinger, K. A.; Laubernds, K.; Son, Y.-C.; Suib, S. L. *Chem. Mater.* **2004**, *16*, 4296. Whitfield, P. S.; Davidson, I. J. *J. Electrochem.* Soc. **2000**, *147*, 4476.

(7) Yan, H.; Huang, X.; Lu, Z.; Huang, H.; Xue, R.; Chen, L. *J. Power Sources* **1997**, *68*, 530. Kalyani, P.; Kalaiselvi, N.; Renganathan, N. G. *J. Power Sources* **2003**, *123*, 53. Nakayama, M.; Watanabe, K.; Ikuta, H.; Uchimoto, Y.; Wakihara, M. *Solid State Ionics* **2003**, *164*, 35. Bao, S.-J.; Liang, Y.-Y.; Zhou, W.-J.; He, B.-L.; Li, H.-L. *J. Power Sources* **2006**, *154*, 239.

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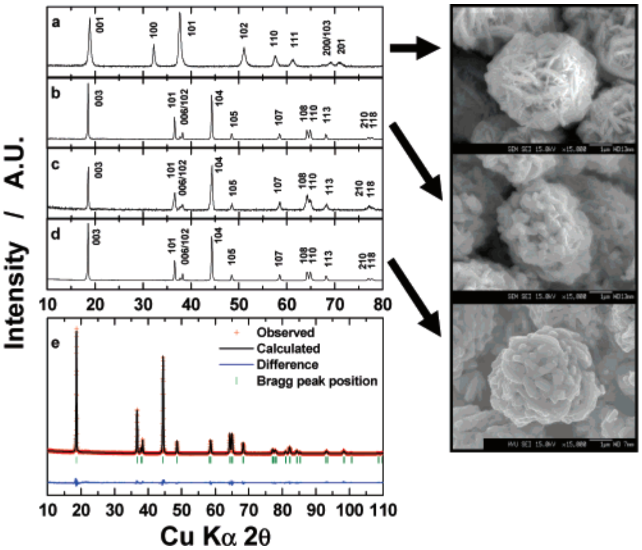

Figure 1. XRD patterns of (a) as-co-precipitated $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$; (b) $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ prepared by high-temperature calcination; (c) $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ synthesized by microwave irradiation (powder mixture); (d) $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ synthesized by microwave irradiation (pelletized powder mixture), and (e) Rietveld refinement of $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ powder (d).

mixture was fired at 900 °C for 15 h in an air. As can be seen in Figure 1b, one can see a well-ordered α-$NaFeO_2$ ($R\bar{3}m$) structure. Peak splittings of (006)/(102) and (108)/(110) pairs are also clear, which is usually observed in a well-developed layer structure. SEM image illustrates a spherical secondary particle with submicrometer-sized primary particle. A powder mixture of $Ni_{0.4}Co_{0.2}Mn_{0.4}(OH)_2$ hydroxide and $LiOH\cdot H_2O$ was irradiated to microwave of 2.45 GHz with 1200 W power for 10 min and the corresponding XRD pattern is shown in Figure 1c. Though widths of diffraction peaks are relatively broader, meaning lower crystallinity compared to Figure 1b, it is obvious that α-$NaFeO_2$ structure was formed by the microwave treatment for 10 min. Peak splittings of (006)/(102) and (108)/(110) pairs are less clear than that in Figure 1b, indicating less-developed layered structural ordering. Under the same condition as Figure 1c, a pelletized powder mixture was also treated by the microwave irradiation. Surprisingly, a well-developed layer structure was formed in Figure 1d by microwave treatment for just 10 min. Also, the peak splittings of (006)/(102) and (108)/(110) pairs are quite as clear as that in Figure 1b, in which the product was obtained by calcination at 900 °C for 15 h. The primary particle size (~1 μm) is larger than that obtained by high-temperature calcination, though the secondary particle size is closer (~4 μm).

In fact, one-step syntheses of lithiated transition metal oxide for lithium-battery grades via microwave irradiation seem to be difficult.[7] To improve the crystallinity of the final product, we didn't dispose of subsequent calcinations at higher temperatures for long times, even after microwave treatments.[7] Repetitive microwave treatments also led to a single-phase product, though the crystallinity of the resulting product was quite poor compared with that of the material produced by conventional solid-state reaction.[7] Most cases, though they employed transition metal oxides or their derivatives for microwave synthesis, could not obtain highly crystalline products via one-step microwave treatment. Usually, transition metal oxides get heated up very fast in microwaves. Nonetheless, further heat treatments at higher temperatures for longer times were necessary to obtain high crystallinity.[7]

Table 1. Structural Parameters Obtained from Rietveld Refinement of XRD Pattern of $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ Synthesized by Microwave Irradiation (pelletized powder mixture)[a]

atom	site	*x*	*y*	*z*	*g*	*B* (Å^2)
Li1	3*a*	0	0	1/2	0.969(2)	0.7
Ni2	3*a*	0	0	1/2	0.031(2)	0.7
Li2	3*b*	0	0	0	0.031	0.9
Ni1	3*b*	0	0	0	0.373(2)	0.9
Mn	3*b*	0	0	0	0.393	0.9
Co	3*b*	0	0	0	0.203	0.9
O	6*c*	0	0	0.258(16)	1	0.8

[a] Formula, $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$; crystal system, hexagonal; space group, $R\bar{3}m$; $R_{wp} = 10.7\%$; $R_p = 8.32\%$.

As mentioned above, synthesis of a large amount of Ni-containing compound usually causes formation of unwanted secondary phases.[5] Thus, it is thought that selection of starting materials is a significantly critical point to produce phase-pure final product. In our case, we employed $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$ and $LiOH\cdot H_2O$ as the starting materials for the microwave synthesis. Though we did not show it here, the same microwave treatment of a powder mixture pellet of NiO, Co_3O_4, and MnO_2 with $LiOH\cdot H_2O$ did not result in pure $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$. Therefore, it was found that using the homogeneous $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$ hydroxide as the starting material was significantly effective for producing the highly crystalline $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$. Furthermore, contact between particles and particles become much more compact in the pellet state lead to the energy dissipation being be minimized in the pellet during microwave irradiation compared with powder state in Figure 1c. Because of the above reason, it was possible to obtain highly crystalline $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ powders by the microwave treatment. The BET result for the $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ synthesized by the microwave was about 1.4 $m^2\ g^{-1}$, which is similar to that of the powder (1.5 $m^2\ g^{-1}$) prepared by high-temperature calcination showing in Figure 1b.

Rietveld refinement of $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ prepared by the microwave treatment (pellet) is shown in Figure 1e and Table 1, respectively. The refinements resulted in a good agreement between the observed and calculated patterns in Figure 3, which satisfies our structural model. Site exchange between Li^+ and Ni^{2+} was about 3.1%, which is close in value to the reported one.[4] $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ obtained by the high-temperature calcination in Figure 1b also had similar cation mixing (~3.2%) in the crystal structure. The calculated lattice parameters were $a = 2.869(4)$ Å and $c = 14.262(7)$ Å, which coincide with the reported values in the literature.[4] From these results, it is found that microwave irradiation enables the one-step synthesis of highly crystalline $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ by using $[Ni_{0.4}Co_{0.2}Mn_{0.4}](OH)_2$ and $LiOH\cdot H_2O$ as the starting materials.

Figure 2 shows continuous charge and discharge curves for $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ synthesized using high-temperature calcination (hereafter referred as HT) shown in Figure 2a and microwave irradiation (hereafter referred as MI) in Figure

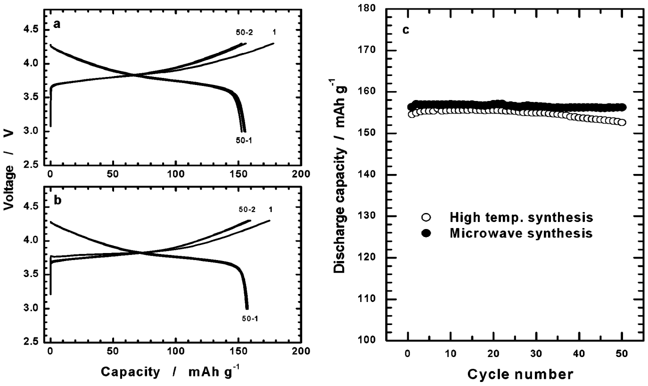

Figure 2. Continuous charge and discharge curves of Li/Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 cells at 30 °C; (a) Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 prepared by high-temperature calcination; (b) Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 synthesized by microwave irradiation (pelletized powder mixture); (c) their corresponding cyclabilities.

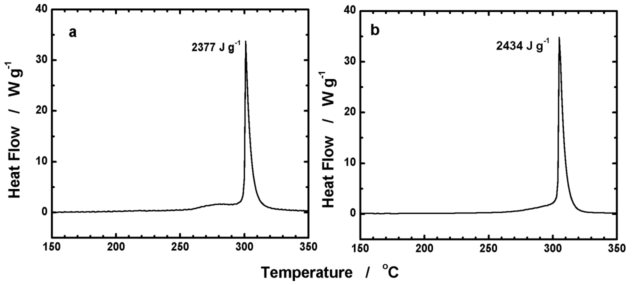

Figure 3. Differential scanning calorimetry (DSC) traces; (a) Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 prepared by high-temperature calcination; (b) Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 synthesized by microwave irradiation (pelletized powder mixture).

2b. Apparently, both samples showed close electrochemical properties in panels a and b in Figure 2. They delivered a specific discharge capacity of about 155−157 mAh (g-oxide)$^{-1}$. After 30 cycles, HT Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 began to show slow capacity fading in Figure 2c. On the other hand, the initial capacity was continuously maintained for the MI-treated Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2. As suggested by Thackeray and Manthiram et al., high-temperature calcination is essentially necessary to obtain good electrochemical properties and maintain its structural integrity during cycling in a lithium secondary battery system.[8] Wakirara et al.[7] reported that higher capacity was seen during several initial cycles for MI-treated $LiMn_2O_4$. However, polarization between charge and discharge voltage was quite large (∼0.2 V on average), which implies that the crystallization process would not be completed. The structure would not be rigid enough to be maintained upon extensive cycling, so that the cycling performance was not so satisfactory. Surprisingly, the MI-treated powders for just 10 min had reasonably higher capacity with excellent cyclability (∼99% retention of its initial capacity) in panels b and c in Figure 2. The charge−discharge curves and operation voltage of MI-treated Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 are almost identical to those of HT Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 in panels a and b of Figure 2. From the above results, it is likely that using homogeneous [$Ni_{0.4}Co_{0.2}Mn_{0.4}$]$(OH)_2$ and $LiOH\cdot H_2O$ as the starting materials were greatly beneficial to improving the crystallinity of the final product, MI-treated Li[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2, and subsequently contributes to the enhancement of electrochemical properties due to the higher crystallinity.

Figure 3 illustrates DSC profiles of delithiated $Li_{0.35}$[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 charged to 4.3 V. The onset temperature of $Li_{0.35}$[$Ni_{0.4}Co_{0.2}Mn_{0.4}$]O_2 was as high as around 305 °C, which is significantly higher than that of $Li_{1-\delta}CoO_2$ (∼190 °C).[9] Because of the presence of tetravalent Mn in the structure, the material showed greatly improved thermal stability in Figure 3. Even though the materials were synthesized via different synthetic routes, the resulting onset temperature of exothermic reaction was similar and even the profiles were close to each other.

From the above results, it is concluded that microwave-irradiation-assisted synthesis using hydroxides was fairly effective at preparing lithiated transition metal oxide within a short time. With the help of homogeneous hydroxide, a one-step, single-phase formation was possible and, as a result, the well-developed highly crystalline oxide was readily formed by means of microwave irradiation, significantly reducing the reaction time and cost. It is believed that this synthetic method would be applicable for almost all kinds of electrode materials for the lithium-battery industry.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Thackeray, M. M. *J. Electrochem. Soc.* **1995**, *142*, 2558. Manthiram, A.; Kim, J. *Chem. Mater.* **1998**, *10*, 2895.

(9) MacNeil, D.; Lu, Z.; Dahn, J. R. *J. Electrochem. Soc.* **2002**, *149*, A1332.