ACS Combinatorial Science

Research Article

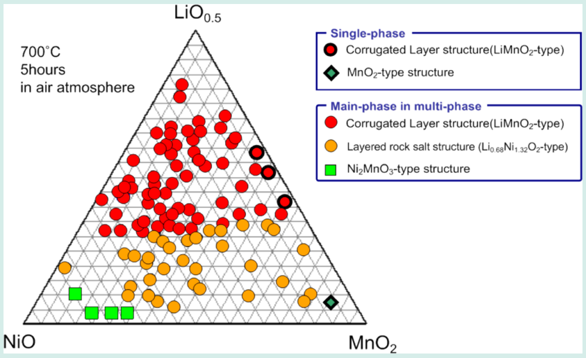
pubs.acs.org/acscombsci

Establishment of Pseudoternary $LiO_{0.5}$−NiO−MnO_2 Phase Diagram by Combinatorial Wet Process

Kenjiro Fujimoto,* Yosuke Shimura, and Shigeru Ito

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Yamazaki 2641, Noda, Chiba 278-8510, Japan

ABSTRACT: A pseudoternary $LiO_{0.5}$−NiO−MnO_2 reaction phase diagram was established using a combinatorial high-throughput materials exploration process to find candidate electrode materials for lithium ion secondary batteries. Each powder library was prepared using our combinatorial wet process based on the electrostatic spray deposition method and results obtained at various firing temperatures in an air atmosphere and an oxide atmosphere. In the air atmosphere, newly composed single phase regions of a layered rock salt-type structure were only found around Li_2MnO_3 at 800 °C. On the other hand, in the oxide atmosphere, most of the powder library showed the multiphase of the spinel and layered rock salt type structure.



KEYWORDS: *spinel structure, layered rock salt structure, corrugated layered structure, reaction phase diagram*

1. INTRODUCTION

Layered rock salt type $LiCoO_2$ is the most commercially used cathode material for lithium ion secondary batteries. $LiCoO_2$, which is prepared using a solid state reaction at more than 800 °C, shows a discharge capacity of about 150 mAh/g and a good cycle performance in the range of 2.5−4.5 V.[1,2] However, the electrode property drops if $LiCoO_2$ must perform charge and discharge in which the output is more than 150 mAh/g because the thermal stability comes down when $LiCoO_2$ is reacted in excess of half of the electron reaction.[3] $LiNiO_2$ have also studied as the cathode materials for lithium ion secondary battery because the crystal structure showed the layered rock salt structure same as $LiCoO_2$. $LiNiO_2$ shows a higher charge−discharge capacity than $LiCoO_2$. However, $LiNiO_2$ shows lower thermal and structure stability than $LiCoO_2$ because amount of the oxygen evolution, which is cause of the electrolyte combustion under temperature up, is larger. To improve the thermal and the structure stability of cathode materials, partially Mn substituted Li−Ni oxides have studied as candidate cathode materials since Mn^{4+} is stable and promising element of preventing the oxygen evolution from structure. And, Yoshio et al. reported that partly Mn-substituted $LiNiO_2$ shows increased stability.[4]

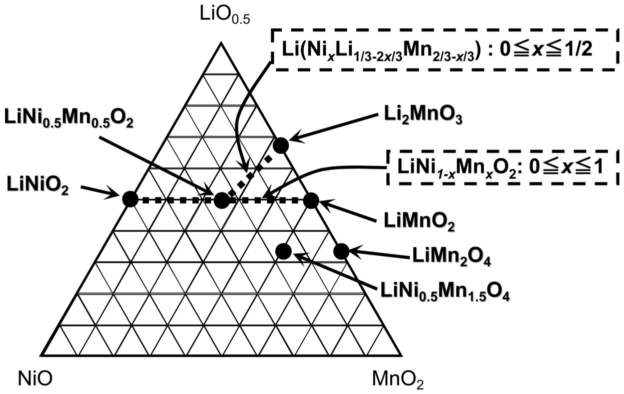


Figure 1. Solid-solution regions in pseudoternary $LiO_{0.5}$−NiO−MnO_2 phase diagram.

In this study, we established reaction phase diagrams on pseudoternary Li−Ni−Mn oxides because some of these oxides are promising cathode materials as they show higher capacity and better cycle performance than $LiCoO_2$. Figure 1 shows the previously reported composition region of single phase of Li−Ni−Mn oxides.[5−8] Among pseudoternary Li−Ni−Mn oxides, layered rock salt-type $LiNi_{0.5}Mn_{0.5}O_2$ and spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ are well-known as cathode materials for lithium ion secondary batteries. $LiNi_{0.5}Mn_{0.5}O_2$ has the same layered rock salt type structure as $LiCoO_2$. $LiNi_{0.5}Mn_{0.5}O_2$ was able to demonstrate greater than 150 mAh/g for its first discharge capacity in the cutoff range of 2.8−4.3 V. The charge−discharge curve of $LiNi_{0.5}Mn_{0.5}O_2$ is very similar to $LiCoO_2$ and $LiNiO_2$, and is able to maintain a cycle performance of more than 95% up to 30 cycles.[9] But it is difficult to prepare excellent electroactive $LiNi_{0.5}Mn_{0.5}O_2$ because its electrochemical properties strongly depend on cation mixing. And, the termal stability is lower than spinel-type $LiNi_{0.5}Mn_{1.5}O_4$. Spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ shows an action potential around 5 V.[10] Therefore, the Li-ion battery electrolyte have to be selected

Received: March 12, 2013
Revised: August 20, 2013
Published: October 30, 2013

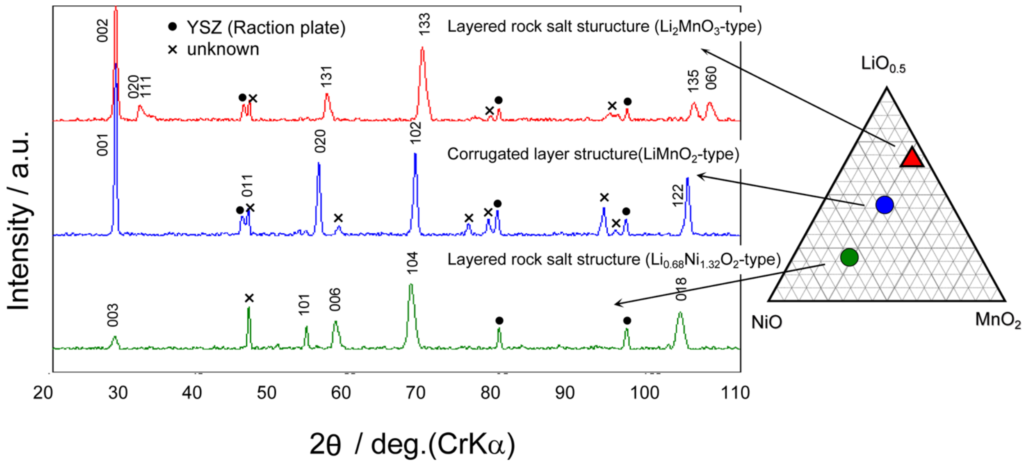


Figure 2. Examples of powder X-ray diffraction patterns in pseudoternary $LiO_{0.5}$−NiO−MnO_2 compounds obtained at 800 °C for 5 h in air atmosphere.

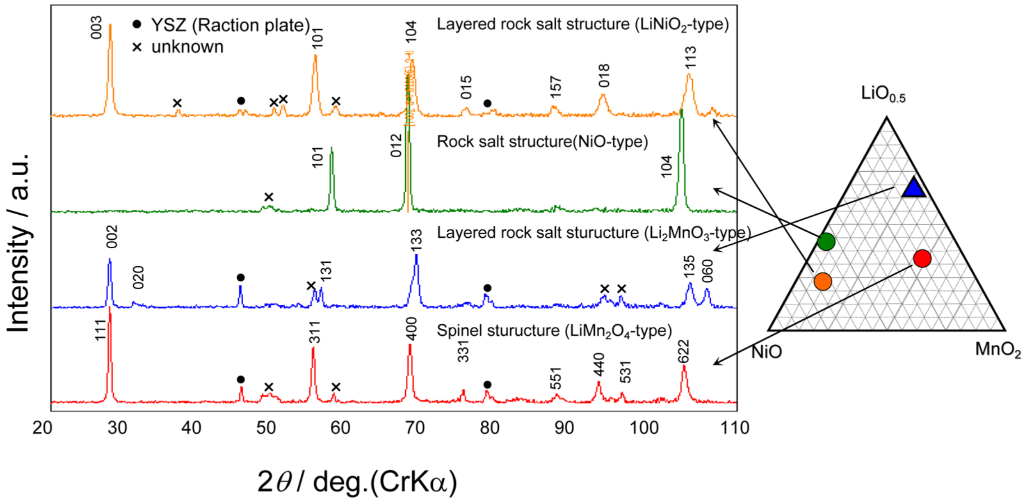


Figure 3. Examples of powder X-ray diffraction patterns in pseudoternary $LiO_{0.5}$−NiO−MnO_2 compounds obtained at 700 °C for 5 h in O_2 atmosphere.

from indissoluble materials. However, its discharge capacity is 110−130 mAh/g and lower than layered rock salt-type $LiNi_{0.5}Mn_{0.5}O_2$. In order to newly explore Li−Ni−Mn oxides which can solve the above-mentioned problems, we tried to establish a pseudoternary $LiO_{0.5}$−NiO−MnO_2 reaction phase diagram and explore new layered rock salt- and spinel-type Li−Ni−Mn oxides using our developed combinatorial high-throughput materials preparation apparatus.[11,12] In addition, Li_2MnO_3 also shows good electrode property. First charge capacity of Li_2MnO_3 was 309 mAh/g at 55 °C.[13] Ni-substututed Li_2MnO_3 type compounds are also promising cathode materials if they are found from the established reaction phase diagram.

2. EXPERIMENTAL PROCEDURES

A pseudoternary $LiO_{0.5}$−NiO−MnO_2 library was prepared using the "M-ist Combi" combinatorial high-throughput materials preparation apparatus based on the electro static spray deposition method. The starting materials used were $LiNO_3$ (99.99%, Aldrich), $Ni(NO_3)_2{\cdot}6H_2O$ (99.999%, Aldrich), and $Mn(NO_3)_2{\cdot}xH_2O$ (99.999%, Aldrich). Each nitrate was adjusted to 0.2 mol/L by the mixing ethanol (C_2H_5OH, 99.5%, Kanto Chemical) and buthyl carbitor ($C_4H_9(OCH_2CH_2)_2OH$, 98.0%, Kanto Chemical). The mixture ratio of ethanol and buthyl carbitor was 1:4. These solutions were set to the M-ist Combi system, and each mixed solution using an applied high voltage, was sprayed from a stainless steel nozzle to the grounded and heated (400 °C) substrate. Each composition ratio of the starting materials was controlled using our developed software. The deposited powder library was then heat-treated at 700−800 °C for 5 h in air or an O_2 atmosphere. The sintered powder library was evaluated using combinatorial X-ray apparatus with Co or Cr−$K\alpha$ radiation. The apparatus consist of an X−Y−Z movable stage and the positive sensitive proportional counter (PSPC). By using two modules, we were able to obtain X-ray diffraction patterns in a short time. The reaction phase diagram of pseudoternary $LiO_{0.5}$−NiO−MnO_2 was established based on the results of identification of the X-ray diffraction pattern and chemical composition analysis. Inductively coupled plasma emission spectroscopy (ICP) was used for the chemical composition analysis.

3. RESULTS AND DISCUSSION

Figure 2 shows examples of powder X-ray diffraction patterns of $(LiO_{0.5})_x$−$(NiO)_y$−$(MnO_2)_z$ ($0 \le x \le 0.8$, $0 \le y \le 1.0$, $0 \le z \le 1.0$, $x + y + z = 1$) which were sintered at 800 °C for 5 h in air

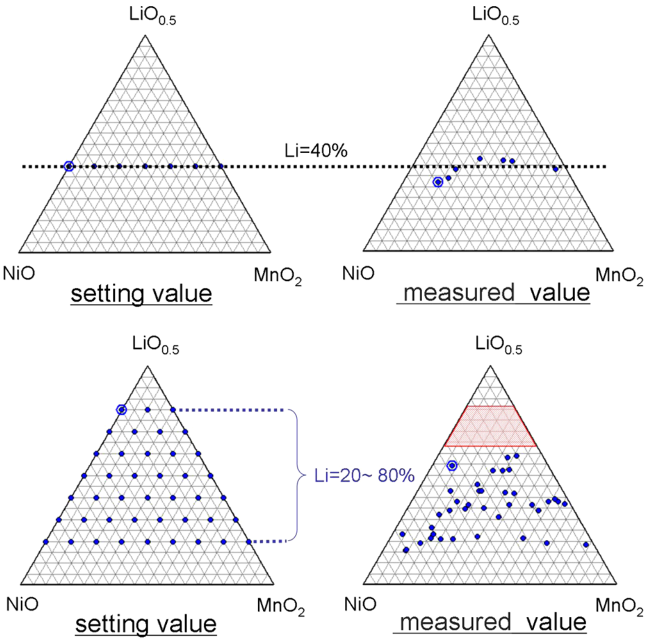


Figure 4. Differences of initial composition condition and result of chemical analysis after heat-treated at 800 °C for 5 h in air atmosphere.

atmosphere. From these X-ray diffraction patterns, we found the layered rock salt-type Li_2MnO_3, $Li_{0.68}Ni_{1.32}O_2$,[14] the corrugated layered-type $LiMnO_2$ and their isomorphs. The single phase composition region of the powder library sintered at 700 °C was only around the previously reported $LiNi_{1-x}Mn_xO_2$ $(0 \leq x \leq 1)$. The single-phase compounds at 800 °C demonstrated not only the single phase composition region of 700 °C but also around Li_2MnO_3. And, most of the powder library included NiO or Ni−Mn oxides as a secondary phase. In addition, Figure 3 shows examples of powder X-ray diffraction patterns of $(LiO_{0.5})_x-(NiO)_y-(MnO_2)_z$ $(0 \leq x \leq 0.8, 0 \leq y \leq 1.0, 0 \leq z \leq 1.0, x + y + z = 1)$ which have been sintered at 700 °C for 5 h in an oxide atmosphere, respectively. From these X-ray diffraction patterns, we found not only $LiNiO_2$- and Li_2MnO_3-type structures but also $LiMn_2O_4$-type, which hadn't been obtained at 700 and 800 °C for 5 h in air atmosphere. However, all powder showing the multiphase also included NiO and MnO_2.

Figure 4 shows the differences of initial composition conditions and results of chemical analysis after heat-treated at 800 °C for 5 h in air atmosphere. In comparison with the initial feed condition of starting materials, the chemical compositions of sintered powder showed a tendency to tilt toward the center part of the reaction phase diagram. The cause of this tendency was due to the working pressure of each syringe pump in the M-ist Combi system as referred to by Fujimoto et al.[11,12] In the initial feed composition condition of $(LiO_{0.5})_x-(NiO)_y-(MnO_2)_z$ $(x = 0.7-0.8, 0 \leq y \leq 0.3, 0 \leq z \leq 0.3, x + y + z = 1)$, the Li component of heat-treated powder decreased more than 10% because a part of the Li element was eliminated in the sintering process.

Figures 5 and 6 show the established reaction phase diagram based on the phase identification of powder X-ray diffraction patterns and the chemical analysis data using ICP apparatus, respectively. The powder library heat-treated at 700 °C in an air atmosphere showed the multiphase as above-mentioned. Also, a layered rock salt type structure was observed under the condition of $x < 0.3$, and a corrugated layered type structure was observed in the region of $x > 0.35$. For the powder library heat-treated at 800 °C, the corrugated layered type structure was observed in the composition region of $x \geq 0.25$. And, single-phase of $LiMnO_2$ type and Li_2MnO_3-type structure were observed.

Figure 7 shows the reaction phase diagram of which the powder library was heat-treated at 700 °C for 5 h in an oxygen atmosphere. There were no new single phase compounds just as with the result observed for the condition of air atmosphere. However, regardless of multiphase, $LiNiO_2$-type and $LiMn_2O_4$-type compounds, which could not observed on the reaction phase diagram at 700 °C for 5 h in air atmosphere, were clearly observed from powder X-ray diffraction patterns. In this study, we could not found single phase of $LiNiO_2$-, $LiMn_2O_4$-, and Li_2MnO_3-type compounds. So, we have to maintain to explore the single phase of these compounds under various sintering temperature.

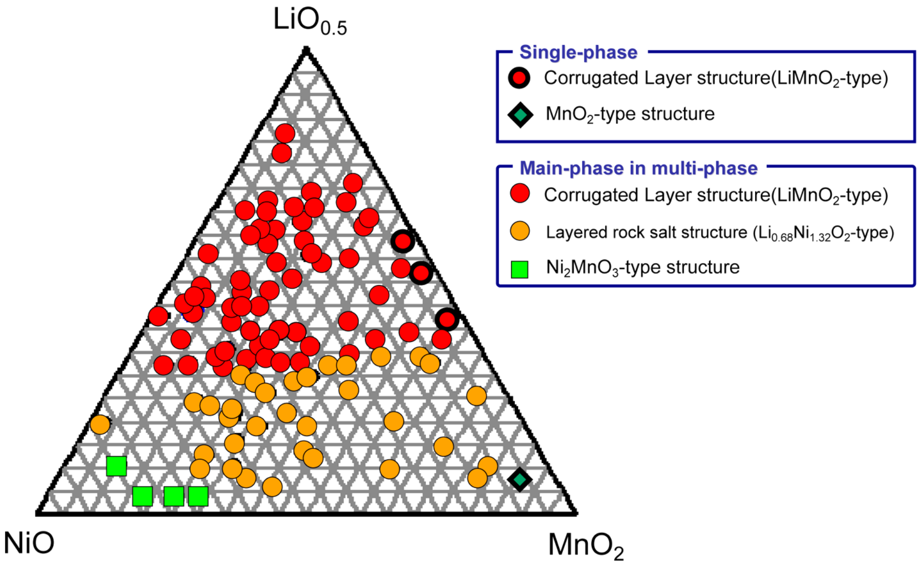


Figure 5. Pseudoternary $LiO_{0.5}-NiO-MnO_2$ reaction phase diagram obtained at 700 °C for 5 h in air atmosphere.

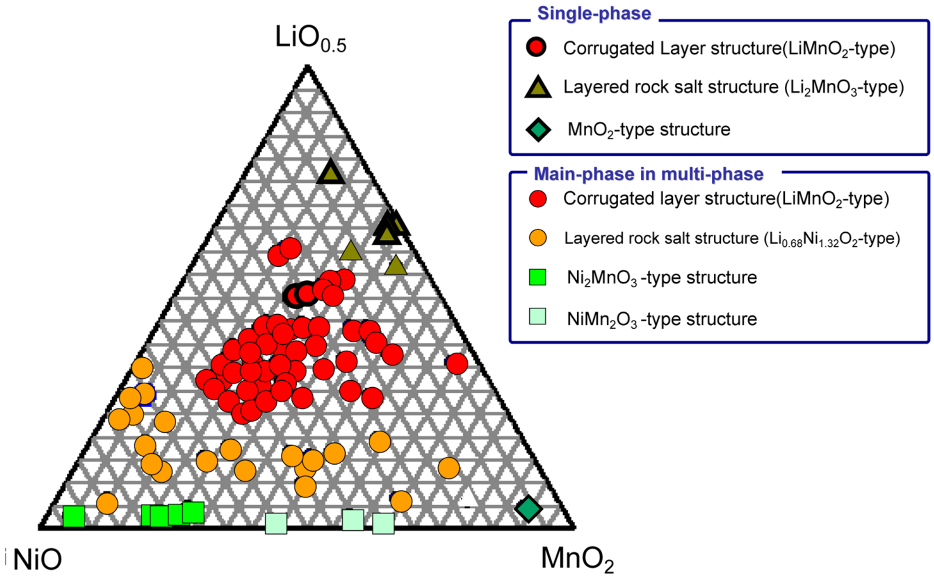


Figure 6. Pseudoternary $LiO_{0.5}$−NiO−MnO_2 reaction phase diagram obtained at 800 °C for 5 h in air atmosphere.

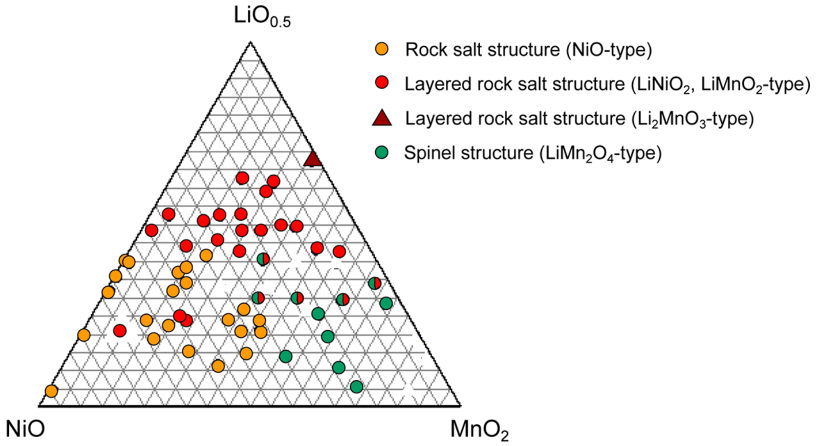


Figure 7. Pseudoternary $LiO_{0.5}$−NiO−MnO_2 reaction phase diagram obtained at 700 °C for 5 h in O_2 atmosphere.

4. CONCLUSIONS

A pseudoternary $LiO_{0.5}$−NiO−MnO_2 powder library was prepared by a M-ist Combi high-throughput materials exploration system based on the electrostatic spray deposition method. We obtained the results under conditions of air or oxide atmosphere. According to the established reaction phase diagram obtained at 700 °C in air atmosphere, most of the powder library showed multiphase containing NiO. A part of powder library obtained at 800 °C in air atmosphere showed single phase for the corrugated layered- and layered rock salt-type structure. On the other hand, for the established reaction phase diagram obtained at 700 °C in an oxide atmosphere, most of the powder library showed multiphase of the spinel- and layered rock salt-type structure.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +81-4-7122-1768. Fax: +81-4-7123-9890. E-mail: fujimoto_kenjiro@rs.tus.ac.jp.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Ohzuku, T.; Ueda, A. Solid-State Redox Reactions of $LiCoO_2$ ($R\bar{3}m$) for 4 V Secondary Lithium Cells. *J. Electrochem. Soc.* **1994**, *141*, 2972−2977.

(2) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. $LixCoO_2$: A New Cathode Material for Batteries of High Energy Density. *Mater. Res. Bull.* **1980**, *15*, 783−799.

(3) Huang, B.; Jang, Y.-I.; Chiang, Y.-M.; Sadoway, D. R. Electrochemical Evaluation of $LiCoO_2$ Synthesized by Decomposition and Intercalation of Hydroxides for Lithium-Ion Battery Applications. *J. Appl. Electrochem.* **1998**, *28*, 1365−1369.

(4) Yoshio, M.; Todorv, Y.; Yamato, K.; Noguchi, H.; Itoh, J.; Okada, M.; Mouri, T. Preparation of $Li_yMn_xNi_{1-x}O_2$ as a Cathode for Lithium-Ion Batteries. *J. Power Sources* **1998**, *74*, 46−53.

(5) Ohzuku, T.; Makimura, Y. Layered Lithium Insertion Material of $LiNi_{1/2}Mn_{1/2}O_2$: A Possible Alternative to $LiCoO_2$ for Advanced Lithium-Ion Batteries. *Chem. Lett.* **2001**, *1*, 744−745.

(6) Ohzuku, T.; Endo, D.; Makimura, T. *Proc. 42nd Battery Symp. Yokohama* **2001**, 118.

(7) Zhong, Q.; Bonakdapour, A.; Zhang, M.; Gao, Y.; Dahn, J. R. Synthesis and Electrochemistry of $LiNi_xMn_{2-x}O_4$. *J. Electrochem. Soc.* **1997**, *144*, 205−213.

(8) Zhang, L.; Noguchi, H.; Yoshio, M. Synthesis and Electrochemical Properties of Layered Li−Ni−Mn−O Compounds. *J. Power Sources* **2002**, *110*, 57−64.

(9) Makimura, Y.; Ohzuku, T. Lithium Insertion Material of $LiNi_{1/2}Mn_{1/2}O_2$ for Advanced Lithium-Ion Batteries. *J.Power Sources* **2003**, *156*, 119−121.

(10) Ohzuku, T.; Ariyoshi, K.; Yamamoto, S.; Makimura, Y. A 3-V Lithium-Ion Cell with $Li[Ni_{1/2}Mn_{3/2}]O_4$ and $Li[Li_{1/3}Ti_{5/3}]O_4$: A Method to Prepare Stable Positive-Electrode Material of Highly Crystallized $Li[Ni_{1/2}Mn_{3/2}]O_4$. *Chem. Lett.* **2001**, *1*, 1270−1271.

(11) Fujimoto, K.; Kato, T.; Ito, S.; Inoue, S.; Watanabe, M. Development and Application of Combinatorial Electrostatic Atomization System M-ist Combi: High-Throughput Preparation of Electrode Materials. *Solid State Ionics* **2006**, *177*, 2639−2642.

(12) Fujimoto, K.; Onoda, K.; Ito, S. Exploration of Layered-Type Pseudo-Four-Component Li−Ni−Co−Ti Oxides. *Appl. Surf. Sci.* **2007**, *254*, 704−708.

(13) Armstrong, A. R.; Robertson, A. D.; Bruce, P. G. Overcharging Manganese Oxides: Existing Lithium beyond Mn^{4+}. *J. Power Sources* **2005**, *146*, 275−280.

(14) Morales, J.; Perez-Vincente, C.; Tirado, J. L. Cation Distribution and Chemical Deintercalation of $Li_{1-x}Ni_{1+x}O_2$. *Mater. Res. Bull.* **1990**, *25*, 623−630.