Hydrothermal Synthesis of Layered Li[$Ni_{0.5}Mn_{0.5}$]O_2 as Lithium Intercalation Material

Seung-Taek Myung, Myung-Hoon Lee,[†] Sang-Ho Park,[†] and Yang-Kook Sun*[†]
VK Corporation, 67 Jije-Dong, Pyongtaek-City, Kyonggi-Do 450-090, Korea
[†]*Department of Chemical Engineering, Hanyang University, Seungdong-Gu, Seoul 133-791, Korea*

(Received March 15, 2004; CL-040288)

In attempt to synthesize layered Li[$Ni_{0.5}Mn_{0.5}$]O_2, a hydrothermal method has been employed. First, the spherical powder precursor, [$Ni_{0.5}Mn_{0.5}$]$(OH)_2$, was prepared via a coprecipitation. Then, the precursor was hydrothermally reacted with an excess amount of LiOH aqueous solution at 170 °C for 4 days. From X-ray diffraction investigation, it was found that the hydrothermally prepared powders showed the layered Li[$Ni_{0.5}Mn_{0.5}$]O_2 having α-$NaFeO_2$ structure (space group: $R\bar{3}m$). The as-prepared powders delivered the initial discharge of about 104 mAh g^{-1}. Further calcination of the hydrothermally prepared powders at 800 °C resulted in the well-ordered layered structure, indicating increase in the crystallinity. Subsequently, the resulting discharge capacity was also improved, 142 mAh g^{-1} by applying a current density of 20 mA g^{-1} (1/8C) and the capacity retention was relatively good during cycling.

LiMO_2 (M = Co, Ni, Mn) is of great interest for application in rechargeable Li-ion battery system. Recently, many research groups focus on the layered Li[$Ni_{0.5}Mn_{0.5}$]O_2, because Mn-based material is essentially cost effective, environmentally kind, and safe.[1,2] The material has a very interesting chemistry; the divalent Ni only participates in the electrochemical reaction from +2 to +4, but the tetravalent Mn^{4+} is electrochemically inactive in the range of 2.7–4.6 V versus Li metal.[3] Instead, the tetravalent Mn supports the layer structure, and therefore, it is possible to keep its original structure during extensive cycling.[4]

To synthesize this material several powder preparation routes were employed such as chimie douce,[4] coprecipitation,[5] spray drying,[6] and so on. Among these methods, the most important concern is how to prepare the homogeneous powder precursor for the synthesis of final product. Of course, most of synthetic methods also adopted high temperature calcination, because the high-temperature heat treatment usually results in high crystallinity and it further causes high capacity and good capacity retention.[8] If not, the resulting capacity and cyclability were disappointing during cycling.[5,6] This problem encouraged us to use the hydrothermal reaction. As we reported previously,[8] the hydrothermal reaction of Mn_3O_4 with excess amount of LiOH gave rise to the well-ordered orthorhombic $LiMnO_2$. The resulting high crystalline orthorhombic $LiMnO_2$ delivered relatively higher capacity upon cycling.

In this work, the metal double hydroxide, ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$, was prepared by a coprecipitation. By the hydrothermal treatment of the precursor at 170 °C, the final product was crystallized to a typical layered structure of α-$NaFeO_2$, Li[$Ni_{0.5}Mn_{0.5}$]O_2. Here, we report on the hydrothermal preparation and electrochemistry of the layered Li[$Ni_{0.5}Mn_{0.5}$]O_2.

Spherical ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$ was prepared as follows; an aqueous solution of $NiSO_4$ and $MnSO_4$ (cationic ratio of Ni:Mn = 1:1) with a concentration of 2.0 mol dm^{-3} was pumped into continuous stirred tank reactor under nitrogen atmosphere. At the same time, NaOH solution (aq) of 2.0 mol dm^{-3} and a desired amount of NH_4OH solution (aq) as an additive were also separately fed into the reactor. At the initial stage of the coprecipitation reaction, the irregular secondary particles from the agglomeration of the acicular primary structure were formed and the irregular particles changed gradually into spherical particles by vigorous stirring for 12 h in the reactor. Then, the spherical ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$ particles were filtered, washed, and dried. The prepared ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$ powders were hydrothermally treated with 3.5 M LiOH aqueous solution at 170 °C for 4 days in autoclaves. A Teflon beaker was used to avoid any reaction with the vessel. After the hydrothermal reaction, the precipitates were washed with deionized water, and the products were dried to remove water at 120 °C in air. X-ray powder diffraction (XRD, Rigaku, Rint 2200) was carried out using Cu Kα radiation to identify the crystalline phases. Scanning electron microscopic observation (SEM, JEOL6400) was carried out using the as-prepared powders. The chemical compositions of the resulting powders were analyzed by atomic absorption spectroscopy (AAS, Vario 6, Analytik Jena AG, Jena, Germany). Charge/discharge cycles were performed in CR2032 coin type cells. The cell consisted of the cathode and the lithium metal anode separated by the porous polypropylene film. For the fabrication of the electrode, the mixture, which consisted of 20 mg of Li[$Ni_{0.5}Mn_{0.5}$]O_2 powders and 5 mg conducting binder (3.3 mg of teflonized acetylene black and 1.7 mg of graphite), was pressed on a 2.0 cm^2 stainless screen at 500 kg cm^{-2}. The used electrolyte was ethylenecarbonate/dimethylcarbonate (1:2 in volume) containing 1 M $LiPF_6$ by volume.

The as-prepared CdI_2 type of layered ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$ by the coprecipitation showed a tone of green color. Ideally, the product has a Ni^{2+} and Mn^{2+} in its oxidation state. In case of room-temperature drying in Figure 1a, it could be observed that the XRD pattern of the powder is almost consistent to the typical fingerprint profile of CdI_2 structure. The absence of impurity phases indicates that Ni and Mn would be homogeneously distributed within ($Ni_{0.5}Mn_{0.5}$)$(OH)_2$ particle. However, the hydrothermal treatment of the hydroxide did not led to the layered Li[$Ni_{0.5}Mn_{0.5}$]O_2 probably owing to the lack of oxidizer, especially not enough oxidation of Mn component, as shown in Figure 1b.

In order to prepare the targeted Li[$Ni_{0.5}^{II}Mn_{0.5}^{IV}$]$O_2$, oxidation of the precursor is necessary, because any oxidizer was not employed during hydrothermal reaction. For oxidation of the Mn, the hydroxide was heated at 110 °C, which brought about change

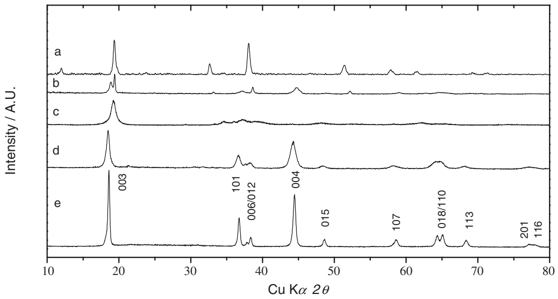

Figure 1. XRD patterns of (a) as-coprecipitated ($Ni_{0.5}Mn_{0.5}$)$(OH)_2$ powders dired at 25 °C, (b) hydrothermal treatment of the as-coprecipitated ($Ni_{0.5}Mn_{0.5}$)$(OH)_2$, (c) ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$ dried at 110 °C, (d) hydrothermal treatment of ($Ni_{0.5}Mn_{0.5}$)$(OH)_x$ dried at 110 °C, and (e) calcination of the hydrothermal products.

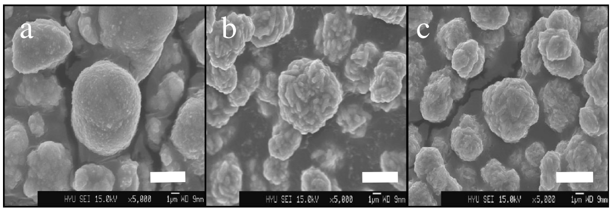

Figure 2. SEM images of (a) $(Ni_{0.5}Mn_{0.5})(OH)_x$ dried at 110 °C, (b) hydrothermally treated $(Ni_{0.5}Mn_{0.5})(OH)_x$ at 170 °C for 4 days, and (c) calcination of the hydrothermal products at 800 °C for 10 h in air. Scale bar means 5 μm.

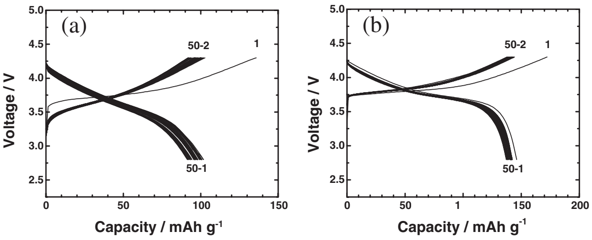

Figure 3. Continuous charge-discharge curves of (a) as-hydrothermally prepared $Li[Ni_{0.5}Mn_{0.5}]O_2$. The sample was calcined at 800 °C for 10 h in air and the results was shown in Figure 3b.

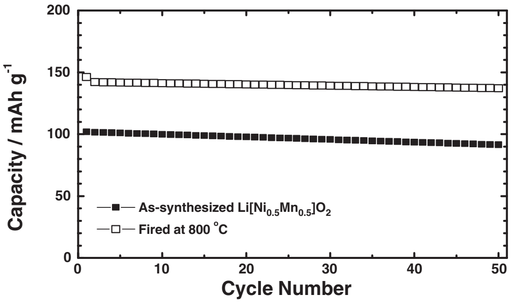

Figure 4. Continuous specific discharge capacity of the prepared powders.

in color to black due probably to the oxidation of Mn to +4. The corresponding XRD pattern is shown in Figure 1c. All the peaks in the Figure 1c are indexed as a mixed phase, such as CdI_2-type and spinel phases. Similar results were reported by Dahn et al.[9] The XRD pattern depicted in Figure 1 is close to the report by Dahn et al.,[9] which means the coexistence of intermediate phase between the CdI_2-type phase and the spinel- type phase. Ooi et al.[11] also described it as a phase with stacked $Ni(OH)_2$ and MnO_2 layers. SEM image of $(Ni_{0.5}Mn_{0.5})(OH)_x$ shows a large number of fine primary crystalline grains in Figure 2a. Most of the secondary particles have the size of 5–10 μm with narrow particle size distribution.

The heat-treated $(Ni_{0.5}Mn_{0.5})(OH)_x$ was hydrothermally reacted with 3.5 M of LiOH aqueous solution at 170 °C for 4 days. The corresponding XRD pattern is shown in Figure 1d. As can be seen in Figure 1b, the hydrothermal reaction led the intermediate phase to the α-$NaFeO_2$ structured $Li[Ni_{0.5}Mn_{0.5}]O_2$ ($R\bar{3}m$), though the crystallinity is relatively low. For the synthesis of $Li[Ni_{0.5}Mn_{0.5}]O_2$, it is common that a high temperature calcination (>900 °C) is necessary to get the $Li[Ni_{0.5}Mn_{0.5}]O_2$ phase. Interestingly, the hydrothermal reaction readily gave the layered $Li[Ni_{0.5}Mn_{0.5}]O_2$ at a temperature as low as 170 °C. The calculated lattice parameters for the as-prepared $Li[Ni_{0.5}Mn_{0.5}]O_2$ were $a = 2.869(6)$ Å and $c = 14.423(12)$ Å by least square method, of which the c-axis value is somewhat higher than reported values.[1–7] This would be ascribed to the low crystallinity of the hydrothermal product. The chemical formula of the hydrothermally prepared powders by atomic absorption spectroscopy is $Li_{1.00}[Ni_{0.49}Mn_{0.5}]O_2$. The particles remains the spherical shape and the average particle diameter is nearly the same as the $(Ni_{0.5}Mn_{0.5})(OH)_x$ even after the hydrothermal reaction, as shown in Figure 2b. That is, the size and shape of the secondary particles hardly changed during the hydrothermal process, and only the primary structure of the particles grow from 0.1 to 0.5 μm, resulting in fine, spherical $Li[Ni_{0.5}Mn_{0.5}]O_2$ powder. It is note worthy that the simple hydrothermal treatment of the coprecipitated $(Ni_{0.5}Mn_{0.5})(OH)_x$ resulted in the layered α-$NaFeO_2$ structure. Details of phase formation mechanism are currently under investigation.

To increase the crystallinity, firing of the hydrothermally prepared $Li[Ni_{0.5}Mn_{0.5}]O_2$ was done at 800 °C for 10 h in an air atmosphere (Figure 1e). The measured lattice parameters as hexagonal setting by Rietveld refinements of XRD data were $a = 2.890(4)$ Å and $c = 14.296(3)$ Å, which are consistent with other reported values in the literatures.[1–7] However, there was no significant change in the particle morphology by the further heat treatment, compared to Figure 2b.

Figure 3 shows the cell voltage profiles plotted versus specific gravimetric capacity for the as-hydrothermally prepared and the heat-treated samples. Comparing with both samples, Li^+ extraction and insertion occurred at a slightly lower voltage for the as-hydrothermally prepared sample in Figure 3a. At the end of discharge, the voltage variation is relatively smooth in Figure 3a, but there was a drastic voltage dropping for the heat-treated sample in Figure 3b. The sample showed a simple voltage variation in the operation range during cycling, of which such behavior is usually observed for lower crystalline electrode materials.[12,13] The obtained capacity after 50 cycles was about 91 mAh g^{-1} for the hydrothermally prepared sample and was 137 mAh g^{-1} for the heat-treated sample in Figure 4.

Although the delivered capacity of the hydrothermally synthesized sample is smaller than that of high-temperature calcination method, the capacity retention was superior to those reported by Caurant et al.[4] and Saphr et al.[5] Further studies to understand the origin of hydrothermal phase formation mechanism will be reported elsewhere in near future. If the mechanism is revealed, it is able to excavate a lot of layered electrode materials by employing this method and it would be applied for lithium-ion battery system.

This work was supported by the Ministry of Information & Communications, Korea, under th Information Technology Research Center(ITRC) Support Program.

References

1 L. Zhang, H. Noguchi, and M. Yoshio, *J. Power Sources*, **110**, 57 (2002).
2 C. S. Johnson, J.-S. Kim, J. Kropf, A. J. Kahaian, J. T. Vaughey, and M. M. Thackeray, *Electrochem. Commun.*, **4**, 492 (2002).
3 X.-Q. Yang, J. Mcbreen, W.-S. Yoon, and C. P. Grey, *Electrochem. Commun.*, **4**, 649 (2002).
4 D. Caurant, N. Baffier, V. Bianchi, G. Gregoire, and S. Bach, *J. Mater. Chem.*, **6**, 1149 (1996).
5 M. E. Spahr, P. Novak, B. Schnyder, O. Haas, and R. Nesper, *J. Electrochem. Soc.*, **145**, 1113 (1998).
6 S.-H. Park, S.-W. Oh, S.-G. Kang, S.-T. Myung, and Y.-K. Sun, *Chem. Lett.*, **33**, 2 (2004).
7 M. M. Thackeray, *J. Electrochem. Soc.*, **142**, 2558 (1995).
8 S.-T. Myung, S. Komaba, and N. Kumagai, *J. Electrochem. Soc.*, **149**, A1349 (2002).
9 S. Jouanneau and J. R. Dahn, *Chem. Mater.*, **15**, 495 (2003).
10 Y. Xu, Q. Feng, K. Kajiyoshi, K. Yanagisawa, X. Yang, Y. Makita, S. Kasaishi, and K. Ooi, *Chem. Mater.*, **14**, 3844 (2002).
11 S. Komaba, N. Kumagai, M. Baba, F. Miura, N. Fujita, H. Groult, and D. Devilliers, *J. Appl. Electrochem.*, **30**, 1179 (2000).
12 M. Baba, N. Kumagai, H. Fujita, K. Ohta, K. Nishidate, S. Komaba, B. Kaplan, H. Groult, and D. Devilliers, *J. Power Sources*, **119–121**, 913 (2003).
13 Z. Lu, L. Y. Beaulieu, R. A. Donaberger, C. L. Thomas, and J. R. Dahn, *J. Electrochem. Soc.*, **149**, A778 (2002).

Published on the web (Advance View) July 5, 2004; DOI 10.1246/cl.2004.818