

## Dispersion of $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ Powder by Surfactant for High-power Li-ion Cell

Su Hyun Yun and Yong Joon Park\*

Department of Advanced Materials Engineering, Kyonggi University, Gyeonggi 443-760, Korea

\*E-mail: yjpark2006@kyonggi.ac.kr

Received April 13, 2009, Accepted June 3, 2009

The particle size of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cathode powder was controlled effectively by dispersion using lauric acid as a surfactant. The samples treated by lauric acid showed smaller particles of approximately half the original size compared to the particles of a pristine sample. A structural change due to the dispersion of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder was not detected. The rate performance of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cathode was improved by dispersion using lauric acid, which was likely due to the decrease of the particle size. In particular, a sample dispersed pristine powder using lauric acid (L2) presented a greatly enhanced discharge capacity and capacity retention at a high C rate. The discharge capacity of a pristine sample was only  $133 \text{ mAhg}^{-1}$  (3C rate) and  $96 \text{ mAhg}^{-1}$  (12C rate) at the tenth cycle. In contrast, the L2 electrode delivered higher discharge capacities of  $160 \text{ mAhg}^{-1}$  (3C rate) and  $129 \text{ mAhg}^{-1}$  (12C rate) at the tenth cycle. The capacity retention at a rate of 12C/2C was also enhanced from  $\sim 45\%$  (pristine sample) to 57% (L2) by treatment with lauric acid.

**Key Words:** Cathode, Battery, Surfactant, Dispersion, Rate performance

### Introduction

The rapid growth in portable electronic devices such as cellular phone, PDA, notebook computer have created enormous activity in the development of advanced lithium secondary battery system. Besides, lithium battery industry has branched out a large size secondary battery market for new application field such as electric vehicles (EVs), hybrid electric vehicles (HEVs), and electric power tools.<sup>1-5</sup> recently. This new application fields are expected to open a huge scale of lithium battery market and develop a related industries.

In order to be used in new application fields, high rate capability of battery system will be an important factor due to the necessity of a fast charge/discharge reaction. In particular, the rate performance of the cathode material has been considered as a bottleneck in the development of lithium secondary batteries with high rate capability. So various of approaches to improve the rate performance of the cathode material have been tried, such as doping of another transition metal,<sup>6,7</sup> addition of a conductive substance such as carbon,<sup>8-10</sup> and decreasing the particle size.<sup>11-19</sup> Among these methods, decreasing the particle size of the cathode powder is one of the ideal methods for increasing the activity of the electrode without capacity loss by additives. The small particle size will accelerate the diffusion of lithium ions between the electrode and the electrolyte and improve the rate capability of the lithium ion cells.

In this current study, we report enhancing the rate capability of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode by decreasing the particle size via dispersion process using lauric acid as a surfactant.  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  is one of the promising cathode materials with a high discharge capacity and stable cyclic performance.<sup>20-22</sup> Lauric acid ( $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ ) is inexpensive, non-toxic, and safe white powder with boiling point of  $298.9^\circ\text{C}$ . It has been used as a surfactant to disperse the powder and decrease the particle size.<sup>12</sup> Such a simple disper-

sion technique using surfactant could be applied easily for obtaining cathode powder with high rate capability without expensive and delicate process.

### Experimental

$\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  was prepared by a simple combustion method from manganese acetate tetrahydrate [ $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ ], nickel(II) nitrate hexahydrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], lithium nitrate [ $\text{LiNO}_3$ ], and lithium acetate dihydrate [ $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ ]. Stoichiometric amount of source materials were dissolved in distilled water and continuously stirred at  $80\text{--}90^\circ\text{C}$  on a hot plate. As the solvent evaporated, the mixed solution turned into a viscous gel. The gel was fired at  $400^\circ\text{C}$  for 1 hr and a vigorous decomposition process occurred resulting in an ash-like powder. The decomposed powder was ground and calcinated at  $500^\circ\text{C}$  for 4 hr and reground. Then, the calcinated powder was treated with different processes. The 'pristine sample' was prepared by heat treatment of obtained powder at  $800^\circ\text{C}$  in air for 7 hr without dispersion process. On the other hand, the sample named 'L1' was dispersed by lauric acid before final heat treatment. At first, 5 wt% of lauric acid and calcinated powder was mixed in the acetone and ball milled for 2 hr, then it was heat treated at  $800^\circ\text{C}$  in air for 7 hr. Lauric acid was removed perfectly during heating process at  $800^\circ\text{C}$ . Another sample named 'L2' was prepared by dispersion of 'pristine sample', 5 wt% of lauric acid and pristine powder was mixed in the acetone and ball milled for 2 hr, and then heat treated at  $800^\circ\text{C}$  for 1 hr.

X-ray diffraction (XRD) patterns of the powders were obtained using a Philips X-ray diffractometer in the  $2\theta$  range of  $15^\circ$  to  $70^\circ$  with monochromatized  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The microstructure of the powder was observed using a FE-SEM (field-emission scanning electron microscopy, JEOL-JSM 6500F). The particle size of the powders was measured by particle size analyzer (Beckman Coulter,

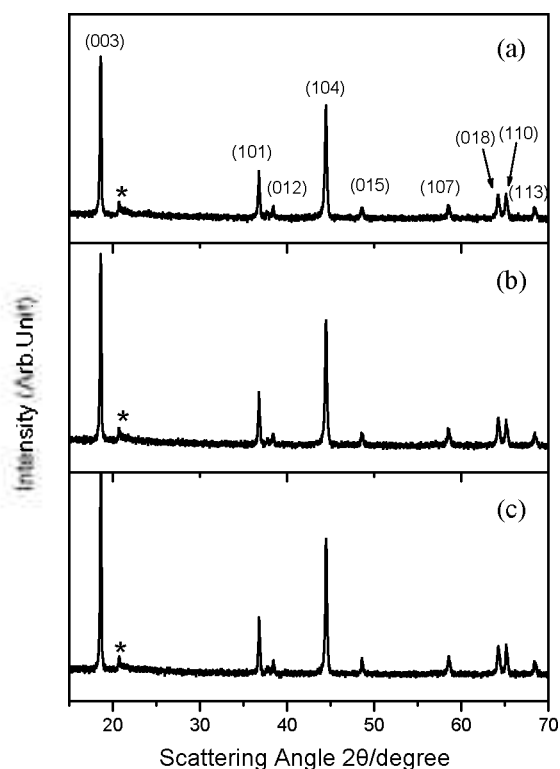
LS230). For the preparation of the cathode electrode, 0.32 g of polyvinylidene difluoride (Aldrich), 3.2 g of the sample powder and 0.48 g of Super P black (MMM Carbon Co.) were mixed with 16 ~ 22 mL of N-methyl-2-pyrrolidone by ball milling system. After 24 hr of ball mill processing, the viscous slurry was coated onto aluminum foil using a Dr. blade then, dried at 90 °C in an oven. The electrochemical cell was assembled in a dry room using above cathode electrode. We used a 1 M  $\text{LiPF}_6$  solution in 1:1 volumetric ratio of ethylene carbonate/dimethyl carbonate as electrolyte. Cells were subjected to galvanostatic cycling using a WonAtech system in the voltage range of 4.8 ~ 2.0 V at various charge-discharge rates of 0.2, 1C, 3C and 12C.

### Results and Discussion

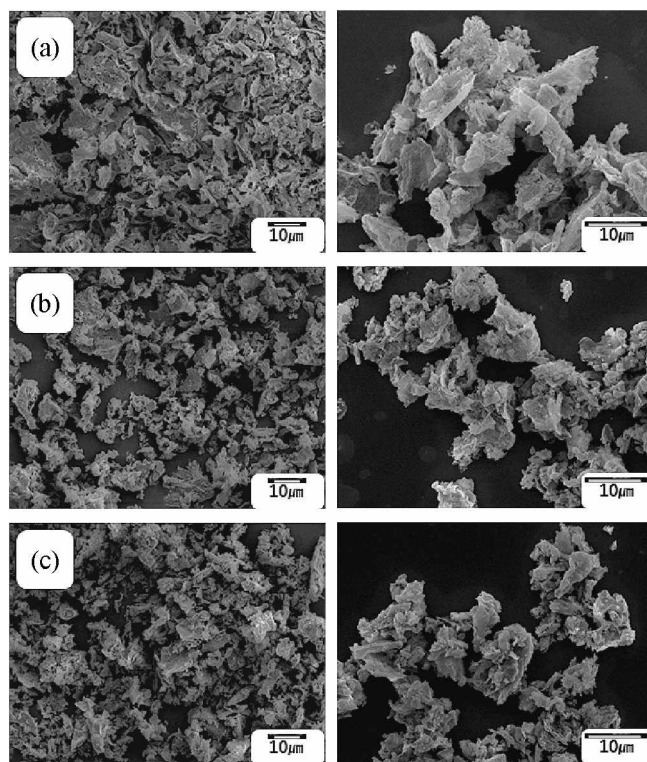
Figure 1 shows X-ray diffraction (XRD) patterns of pristine and dispersed  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powders. The diffraction patterns of all samples are indexed well with that of a typical  $\alpha\text{-NaFeO}_2$  structure (space group R-3m). The small peaks at around 22° (marked as \*) are attributed to the superlattice ordering of Li and Mn in the transition-metal containing layers. The special difference in the phase upon treatment with lauric acid was not detected in the diffraction pattern. The phase of the L2 sample was expected to be identical to that of a pristine sample, as it was dispersed by lauric acid after a final heat treatment at 800 °C. While, the L1 sample was fabricated through dispersion of calcinated (500 °C) powder with a final heat treatment at 800 °C. If the cation ions of Mn, Li and Ni are not mixed homogeneously in the

calcinated powder and are mainly mixed through the final heat treatment by diffusion, the dispersion of the calcinated powder can have a negative effect on the formation of the homogeneous phase because the diffusion of the cation ions during the final heating process is hindered by the dispersion of the primary particles. However, the diffraction pattern of the L1 sample did not show any possibility of a phase change by the lauric acid treatment, although the inhomogeneous cation mixing of the domain scale cannot be ruled out.

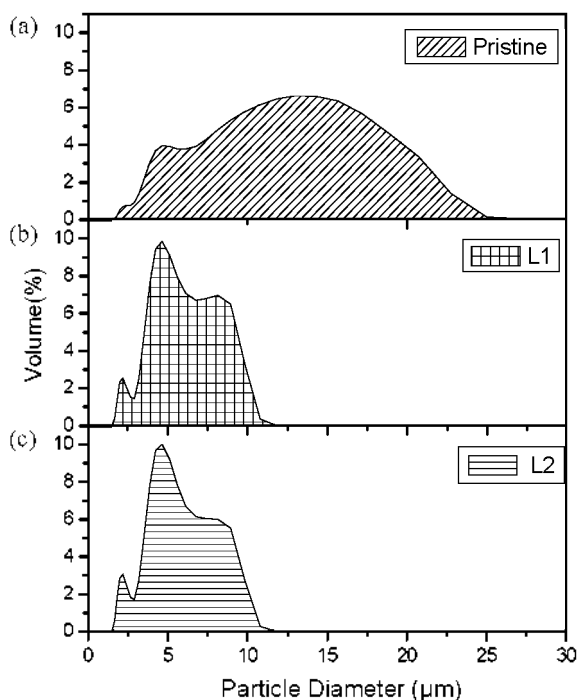
Figure 2 presents scanning electron microscopy (SEM) images of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powders. Essentially, the shape of the particles was very similar regardless of the lauric acid treatment. However, in the more highly magnified image on the right side of Figure 2, the untreated pristine sample contains particles of various sizes. Particularly, largely agglomerated particles were easily found in the pristine powder. On the other hand, the L1 and L2 samples, dispersed by lauric acid, were composed of relatively uniform-sized particles. To confirm these results, the particle size distribution was measured by a particle size analyzer as shown in Figure 3 and Table 1. The size of the pristine powder was distributed in the 1 ~ 20  $\mu\text{m}$  range and only ~ 50% of the powder was found to be smaller in size than 10  $\mu\text{m}$ . However, the particle size was clearly decreased by dispersion using lauric acid. Most of the particle sizes of the L1 and L2 samples were below 10  $\mu\text{m}$  and approximately 50% of the powder was smaller than 5  $\mu\text{m}$ . The size distribution was also narrow within a range of 1 ~ 10  $\mu\text{m}$ . These results show that dispersion by treatment with lauric acid is a suitable method for effective control of the particle size of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder fabricated in a simple



**Figure 1.** XRD patterns of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powders. (a) Pristine; (b) L1; (c) L2. The star (\*) indicates the superlattice ordering peak.



**Figure 2.** SEM images of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powders. (a) Pristine; (b) L1; (c) L2.



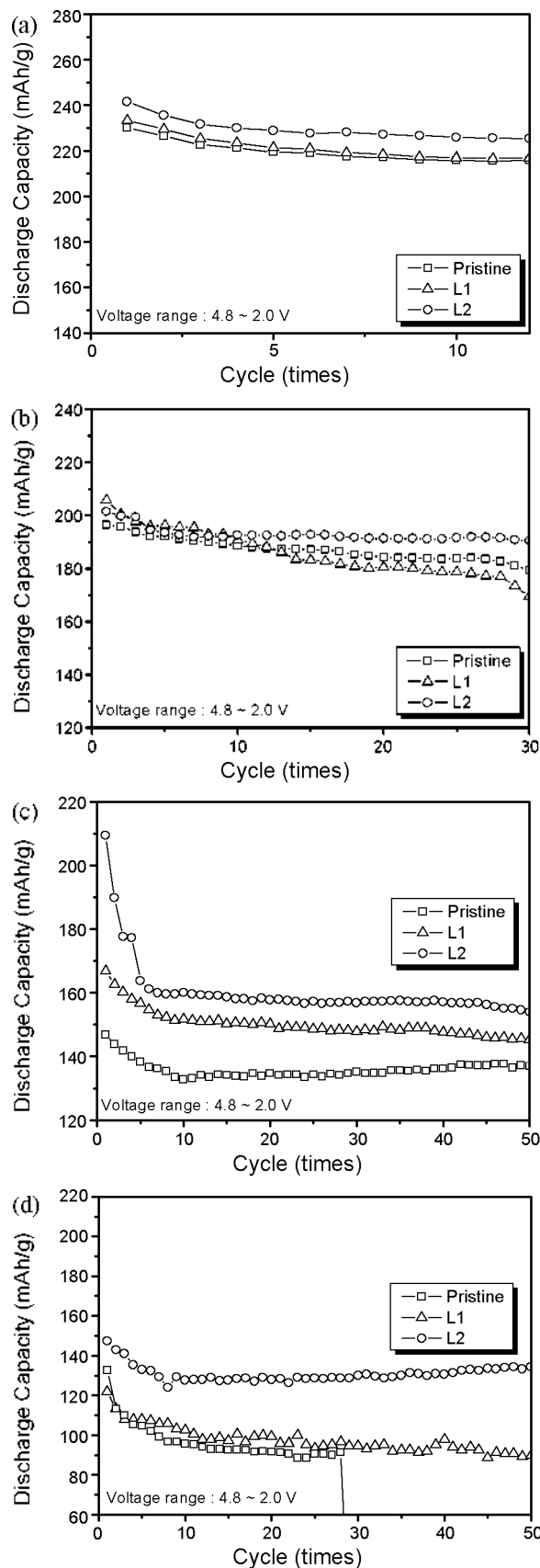
**Figure 3.** Particle size distribution of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powders. (a) Pristine; (b) L1; (c) L2.

**Table 1.** Particle size distribution of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  samples. The value is maximum particle size at each selected part (%) of measured powder.

sample	< 10%	< 25%	< 50%	< 75%	< 90%
Pristine	4.21 $\mu\text{m}$	6.10 $\mu\text{m}$	10.26 $\mu\text{m}$	14.86 $\mu\text{m}$	18.67 $\mu\text{m}$
L1	2.91 $\mu\text{m}$	4.17 $\mu\text{m}$	5.35 $\mu\text{m}$	7.30 $\mu\text{m}$	8.95 $\mu\text{m}$
L2	2.59 $\mu\text{m}$	4.00 $\mu\text{m}$	5.13 $\mu\text{m}$	6.94 $\mu\text{m}$	8.75 $\mu\text{m}$

combustion method. Powder prepared by a combustion process consists of aggregates of small primary particles with size in the range of 50 ~ 100 nm.<sup>23</sup> Although the primary particle was very small, the particle size of the powder was increased due to the sintering effect of the primary particle during the final heating process. The small particle size of the L1 sample indicates that lauric acid mixed with calcinated powder successfully reduces the sintering effect of the primary powder on the particle size. On the other hand, the L2 sample was prepared by dispersion of a pristine sample using lauric acid, although subsequent heat treatment at 800 °C for 1 hr was added to prevent contamination by water and to remove stress during the mixing process. On average, the L2 particles were approximately half the size of a pristine particle, and those were even smaller than the L1 particles, showing that lauric acid treatment is also effective for the dispersion of pristine powder as well as calcinated powder.

To investigate the effect of the particle size of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powders on the rate performance, the discharge capacity and cyclic performance were measured at various C rates in a voltage range of 4.8 ~ 2.0 V. As mentioned in earlier studies,<sup>20,23</sup> the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  compound shows a flat voltage plateau at 4.4 ~ 4.6 V during the initial charge process



**Figure 4.** Discharge capacity and cyclic performance of  $\text{Li}/\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cells cycled between 4.8 and 2.0 V at a specific current of (a) 40  $\text{mAhg}^{-1}$  (0.2C rate); (b) 200  $\text{mAhg}^{-1}$  (1C rate); (c) 600  $\text{mAhg}^{-1}$  (3C rate); (d) 2400  $\text{mAhg}^{-1}$  (12C rate).

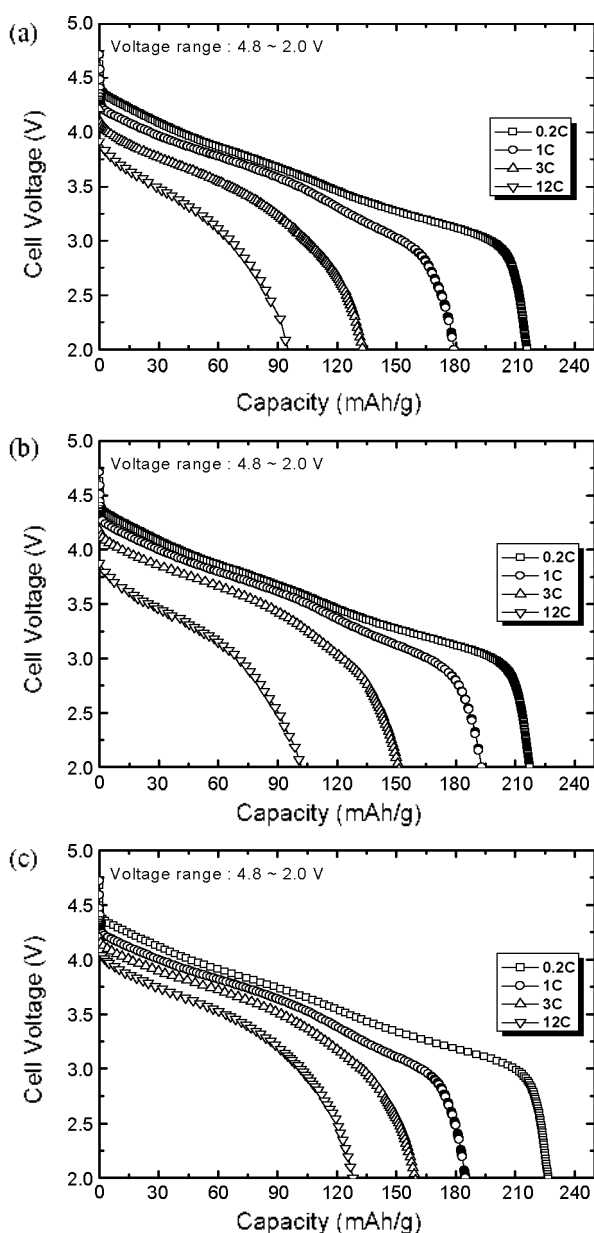
due to an irreversible reaction. To remove the effect of the irreversible reaction during the first cycle, all of the test cells were initially charged and discharged at a 0.2C rate and were then cycled at 0.2C, 1C, 3C and 12C rates, respectively. In this study, the electrochemical data is described from the second cycle without the initial cycle.

Figures 4a and 4b show the discharge capacity and cyclic performance of cells containing  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrodes at 0.2C and 1C rates. At both C rates, the discharge capacities of the L1 and L2 electrodes were somewhat higher compared to that of a pristine electrode, but the difference in the capacity was not great. As shown in Figures 4c and 4d, however, the effect of the particle size was more prominently observed at the high charge-discharge rate of 3C and 12C. The

L1 and L2 electrodes delivered higher discharge capacity than a pristine electrode, which clearly indicates that a decrease in the particle size can enhance the rate capability of a  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode. Lauric acid is an organic material, so it contains carbon (C) in the structure, which implies that it can be a source of residual carbon after lauric acid treatment. Thus it could be suspected that enhanced rate capability was not attributed to the particle size effect but due to the residual carbon originated from lauric acid. However,  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  was heat treated at 800 °C under air condition, so the carbon would be totally evaporated as gas ( $\text{CO}_2$ ). Moreover, we tested lauric acid with heating at 400 °C for 1h under air condition and confirmed that it was totally removed without residual carbon. Some cathode electrode such as  $\text{LiFePO}_4$  has tried carbon coating using various organic materials. However,  $\text{LiFePO}_4$  was heat treated under inert atmosphere, so the carbon coating layer originated from organic materials could be remained in the structure. In contrast,  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  was heat treated under air condition at 800 °C, the amount of residual carbon would be negligible.

Figure 5 displays the tenth discharge profiles of the pristine, L1 and L2 electrodes at 0.2C, 1C, 3C and 12C rates in comparison of the rate performances of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrodes. In Figure 4, the rapid capacity fading of the samples during several initial cycles, especially at a high C rate, was investigated; the tenth cycle was chosen for a comparison of the stabilized discharge capacity of the samples. The pristine, L1 and L2 electrodes displayed discharge capacities of 216  $\text{mAhg}^{-1}$ , 217  $\text{mAhg}^{-1}$  and 226  $\text{mAhg}^{-1}$ , respectively, at a rate of 0.2 C. With the increase in the C rate, the discharge capacities of all samples decreased as was expected; however, the L1 and L2 electrodes showed superior capacity retention at a high C rate. The pristine sample displayed a relatively small discharge capacity of 133  $\text{mAhg}^{-1}$  and 96  $\text{mAhg}^{-1}$  at 3C and 12C rates. The capacity retention at a rate of 3C/0.2C and 12C/0.2C, as calculated by the value of the tenth cycle, was only ~61% and ~45%, respectively. However, the L1 and L2 samples delivered higher discharge capacities of 151  $\text{mAhg}^{-1}$  and 160  $\text{mAhg}^{-1}$ , respectively, at a rate of 3C. The capacity retention (tenth cycle) at a rate of 3C/0.2C also reached ~70%. At a 12C rate, L2 showed a higher discharge capacity (129  $\text{mAhg}^{-1}$ ) and capacity retention (57%). L1 also showed an enhanced discharge capacity and better capacity retention than the pristine sample; however, these values were a slightly inferior to those of L2. Table 2 summarizes the discharge capacity and capacity retention of the three samples at various C rates.

In lines with these results, it is clear that the dispersion of



**Figure 5.** Discharge profile of the  $\text{Li}/\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cells cycled between 4.8 and 2.0 V at 0.2C, 1C, 3C and 12C rates. (a) Pristine; (b) L1; (c) L2.

**Table 2.** Discharge capacity and capacity retention of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  samples at various specific current densities (values of the 10<sup>th</sup> cycle). (%) indicates capacity retention compared to discharge capacity at 0.2C rate.

C rate	Pristine (mAh/g)	(%)	L1 (mAh/g)	(%)	L2 (mAh/g)	(%)
0.2C	216.05	100.0	217.33	100.0	226.70	100.0
1C	189.29	87.6	193.06	88.8	191.91	84.7
3C	133.51	61.8	151.37	69.6	159.63	70.4
12C	96.64	44.7	103.20	47.5	129.35	57.1

powder using lauric acid can effectively enhance the rate performance of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrodes. due to the decrease of the particle size. The small particle size implies a short diffusion pathway for lithium ions and electrons, facilitating the movement of electrons and lithium ions during the charge and discharge processes. In particular, this phenomenon will be more prominent at high C rates. The superior rate performance of L2 to that of L1 suggests that the dispersion of pristine powder after the final heat treatment is superior to the dispersion of calcinated powder before the final heat treatment. It is possible that the dispersion of calcinated powder before formation of a stable phase can deteriorate the homogeneity of cation mixing somewhat and have a negative effect on the discharge capacity. The different heating process is attributable to the crystallinity and electrochemical properties of the samples.

### Conclusions

Lauric acid was used as a surfactant to control the particle size of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder prepared in a simple combustion method. A sample termed L1 was fabricated by dispersion of calcinated powder using lauric acid and subsequent heat treatment at 800 °C. A sample denoted as L2 was prepared by dispersion of a pristine sample after a final heat treatment. The particle size of both samples was clearly decreased. The size of the pristine powder was distributed in the range of 1 ~ 20  $\mu\text{m}$ , while, the most of the particles of the L1 and L2 samples were less than ~ 10  $\mu\text{m}$  in size. The rate performance of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  electrode was improved by dispersion using lauric acid, which was attributed to the decrease of the particle size. Compared with the values of the tenth cycle, the pristine sample displayed a relatively small discharge capacity of 133  $\text{mAhg}^{-1}$  and 96  $\text{mAhg}^{-1}$  at rates of 3C and 12 C, respectively. However, L2 delivered higher discharge capacities of 160  $\text{mAhg}^{-1}$  (a 3C rate) and 129  $\text{mAhg}^{-1}$  (a 12 C rate). The capacity retention at a rate of 12C/2C was as high as ~ 57%, whereas that of the pristine sample was only ~ 45%. The L1 sample also showed better rate performance than the pristine sample, whereas the L2 sample presented a greatly superior property in this regard, which indicates that dispersion of the powder after the formation of a stable structure would be better for enhancing

the rate performance compared to dispersion of only calcinated powder with a subsequent final heat treatment.

**Acknowledgments.** This work was supported by the Korean Ministry of Information and Communication.

### References

- Huang, S.; Wen, Z.; Yang, X.; Gu, Z.; Xu, X. *J. Power Sources* **2005**, *148*, 72.
- Zhang, S.; Qiu, X.; He, Z.; Weng, D.; Zhu, W. *J. Power Sources* **2006**, *153*, 350.
- Amine, K.; Liu, J.; Belharouak, I.; Kang, S. H.; Bloom, I.; Vissers, D.; Henriksen, G. *J. Power Sources* **2005**, *146*, 111.
- Park, Y. J.; Lee, J. W.; Lee, Y.-G.; Kim, K. M.; Kang, M. G.; Lee, Y. *Bull. Korean Chem. Soc.* **2007**, *28*, 2226.
- Ryu, J. H.; Kim, S. B.; Park, Y. J. *Bull. Korean Chem. Soc.* **2009**, *30*, 657.
- Wang, X.; Tanaike, O.; Kodama, M.; Hatori, H. *J. Power Sources* **2007**, *168*, 282.
- Shin, Y.; Manthiram, A. *Electrochem. Solid State Lett.* **2003**, *6*, A34.
- Cushing, B. L.; Goodenough, J. B. *Solid State Sci.* **2002**, *4*, 1487.
- Doeff, M. M.; Wilcox, J. D.; Kostecki, R.; Lau, G. *J. Power Sources* **2006**, *163*, 180.
- Kim, J. S.; Kim, B. S.; Lee, J. G.; Cho, J. P.; Park, B. W. *J. Power Sources* **2005**, *139*, 289.
- Meligrana, G.; Gervaldi, C.; Tuel, A.; Bodoardo, S.; Penazzi, N. *J. Power Sources* **2006**, *160*, 516.
- Choi, D. W.; Kumta, P. N. *J. Power Sources* **2007**, *163*, 1064.
- Chen, H.; Qiu, X.; Zhu, W.; Hagenmuller, P. *Electrochem. Commun.* **2002**, *4*, 488.
- Huang, H.; Yin, S. C.; Nazar, L. F. *Electrochem. Solid State Lett.* **2001**, *4*, A170.
- Kim, D. H.; Kim, J. *Electrochem. Solid State Lett.* **2006**, *9*, A439.
- Kim, J. S.; Johnson, C. S.; Vaughey, J. T.; Hackney, S. A.; Walz, K. A.; Zeltner, W. A.; Anderson, M. A.; Thackeray, M. M. *J. Electrochem. Soc.* **2004**, *151*, A1755.
- Xia, Y.; Yoshio, M.; Noguchi, H. *Electrochim. Acta* **2006**, *52*, 240.
- Leising, R. A.; Palazzo, M. J.; Takeuchi, E. S.; Takeuchi, K. J. *J. Electrochem. Soc.* **2001**, *148*, A838.
- Maleki, H.; Hallaj, S. A.; Seiman, Jr.; Dinwiddie, R. B.; Wang, H. *J. Electrochem. Soc.* **1999**, *146*, 947.
- Hong, Y. S.; Park, Y. J.; Ryu, K. S.; Chang, S. H.; Kim, M. G. *J. Mater. Chem.* **2004**, *14*, 1424.
- Lu, Z.; Dahn, J. R. *J. Electrochem. Soc.* **2002**, *149*, A1454.
- Lu, Z.; Dahn, J. R. *J. Electrochem. Soc.* **2002**, *149*, A815.
- Park, Y. J.; Hong, Y. S.; Wu, X. K.; Ryu, S.; Chang, S. H. *J. Power Sources* **2004**, *129*, 288.