Li-rich layered cathode microparticle

0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ decorated with nanosized grains

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A lithium-rich layered cathode material [0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂] containing nanosized grains (50–100 nm) was prepared from an aqueous precursor solution via a sequential two-step process composed of ultrasonic spray pyrolysis and post-calcination. The microsized lithium-rich layered composites show a high initial discharge capacity of 251 mAh g⁻¹ at 0.1 C. The reversible capacities of 206 mAh g⁻¹ at 0.5 C and 189 mAh g⁻¹ at 1 C are obtained between 4.6 and 2.0 V. These are comparable to the values reported previously for these materials, without the need for doping or surface modification. The improved electrochemical performance may have resulted from the presence of nanosized grains, which can lead to an improvement in electronic and ionic transport, and the homogeneously dispersed Li₂MnO₃ phase in the LiMO₂ (M = Mn, Ni, Co) phase. These results suggest that spray pyrolysis is an effective technique for the preparation of multi-component composite materials and can be used to control the microstructure of the materials, ultimately improving the electrical performance.

Key-words : Layered oxide cathode, Electrochemical performance, Energy efficiency, Spray pyrolysis, Lithium-ion battery

1. Introduction

Coping with climate change has become one of the most important issues of this era. In this regard, many researchers in various fields have worked on the sequestration of greenhouse gases.¹¹ Transportation sector accounts for almost 14% of global greenhouse gas emissions. Therefore, replacing fossil fuel-based vehicles with electric vehicles is a key strategy to reducing greenhouse gas emissions. This need promotes the development of high-capacity energy storage systems.²² Among the various types of batteries, lithium-ion batteries are considered the most attractive option because of their light weight and high power density.³⁻⁵ However, current performance is not satisfactory for the full-scale commercialization of electric vehicles (EVs) and hybrid electric vehicles (HEVs).⁶ Increasing the driving range and reducing battery costs remain key issues that need to be addressed.

Li-rich layered cathode materials 𝑥Li₃MnO₂·(1−𝑥) LiMO₂ (M = Ni, Co, Mn) are gaining popularity because of their high capacities, broad voltage range (~4.6 V), low cost, and high stability⁷⁻¹³ compared to commercial LiCoO₂.¹⁴,¹⁵ However, layered 𝑥Li₃MnO₂·(1−𝑥) LiMO₂ shows a low-rate capability because of its low electronic conductivity, which is caused by the insulating Li₂[LiₓMn₁₋ₓ]O₂ component.¹⁶⁻¹⁸ Therefore, the low-rate capabilities of these batteries need to be improved for their use in EVs and HEVs, which require fast charge/discharge reactions.

Various methods have been developed to enhance the rate capability of Li-rich layered cathode materials such as heteroatom doping, surface modification, and coating.¹⁴,¹⁶,¹⁷ However, attempts to control the morphology and particle size have rarely been accomplished because of limitations of preparation methods. The cathode materials are normally prepared by solid-state reactions or liquid-phase methods requiring a high calcination temperature and long calcination time to obtain the desired composite phase.¹⁸⁻²⁰ These calcination conditions result in the aggregation and growth of primary particles, which disrupt the diffusion of Li-ions between the electrode and the electrolyte.

In recent studies, spray pyrolysis has attracted attention for the fabrication of multicomponent ceramic particles owing to its prominent advantages of simplicity, controllability, and capability to produce particles with high crystallinity.²¹⁻²⁴ In this study, we prepared spherical 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles containing nanosized grains by spray pyrolysis and a post heat treatment. Additionally, the structural and electrochemical properties of the prepared microparticles were investigated.

2. Experimental procedure

2.1 Preparation of Li-rich layered cathode micro particles

Spray pyrolysis process was used to produce Li-rich layered oxide microparticles of the cathode material, 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂. The detailed description of this
process was presented in our previous report.25) The reaction temperature and flow rate of the carrier gas (air) were fixed at 800°C and 15 L/min, allowing the residence time of precursor droplets in the reactor to be 1.6 s. The concentration of the aqueous precursor solution was adjusted to 0.5 mol L⁻¹ of the title compound with suitable quantities of lithium nitrate (LiNO₃, 98%, Junsei), manganese nitrate [Mn(NO₃)₂·6H₂O, 98%, Kanto], nickel nitrate [Ni(NO₃)₂·6H₂O, 98%, Junsei], and cobalt nitrate [Co(NO₃)₂·6H₂O, 97%, Junsei]. The microparticles prepared by this process were calcined at temperatures between 600 and 1000°C for 12 h to understand the effect of calcination on cycle stability and rate capability.

2.2 Characterization of Li-rich layered cathode microparticles

The crystal structures of the 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles were confirmed by X-ray diffractionmetry [XRD; Rigaku, D/Max-2500 (18 kW)] with filtered CuKα radiation. The Brunauer–Emmett–Teller technique (BET; Micrometrics, ASAP2010) was employed to measure the total surface area of the microparticles. The size distribution was obtained using a particle size analyzer (Cilas, 1064). The morphological properties were analyzed by field-emission scanning electron microscopy (FE-SEM; HITACHI, S-4800) and field-emission transmission electron microscopy (FE-TEM; FEI, Tecnai G2 F30). The thermal properties of the microparticles were determined by thermogravimetry-differential scanning calorimetry (TG-DSC; Setaram, Setsys 16/18).

The slurry for preparing the electrode was composed of the active material (88 wt%), polyvinylidene difluoride (5.5 wt%), and carbon black (Denka, 6.5 wt%). The slurry was cast on aluminum foil and dried at 130°C for 30 min. The electrode was pressed with a rolling machine to obtain a material with a porosity of 33% and then punched into 15-mm-diameter disks. Lithium foil (Hohnsen Corporation) was used as the negative electrode and the electrolyte solution was 1 M LiPF₆ in solvent. All procedures used to prepare the cell were performed in a dry room. The assembled cells were aged for 24 h before the first charge to ensure full absorption of the electrolyte into the electrode. Electrochemical performances were evaluated between 4.6 and 2.0 V at 25°C using a TOSCAT 3100 series electrochemical bench. For rate capability, various current rates (0.1, 0.2, 0.5, 1, and 2 C; where 1 C = 200 mA h g⁻¹) were applied. After rate capability measurements, the cycle stability was evaluated at a rate of 0.5 C.

3. Results and discussion

The microparticles prepared by spray pyrolysis have a spherical morphology with a mean diameter of 1.59 μm (Fig. 1). The TG-DSC curves of the microparticles show three weight-loss regions (Fig. 2). The first weight-loss region observed at a temperature below 150°C is related to the evaporation of water molecules adsorbed on the precursor particles. The second weight-loss step (150–600°C) is attributed to the decomposition of nitrate precursors and the formation of the LiMO₂ (M = Ni, Co, Mn) phase. The last step is speculated to be the formation of the Li₃MnO₃ phase, which will be explained later in the paper using XRD results (Fig. 5). The total weight loss was about 10 wt%.

Fig. 1. (a) SEM images and (b) particle size distribution of as-prepared 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles via spray pyrolysis process.

Fig. 2. TG/DSC curves of as-prepared 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles.

occur. Because, the post-heat treatment condition in this study is very mild compared to those in literatures, leading to significant loss of lithium content.26) The SEM and TEM images of the 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles calcined at different temperatures are presented in Fig. 3. The microparticles calcined at 700°C were aggregate-free and had a morphology similar to that of the as-prepared microparticles. Grain growth of the primary particles—nanosized grains having diameters ranging from 10 to 50 nm—
The mean particle size increased from 1.92 to 3.59 μm, indicating a decrease in surface area at the calcination temperature of 800°C. When the temperature was increased from 700 to 1000°C, there was a dramatic drop in the surface area at the calcination temperature of 800°C. The mean particle size increased from 3.59 to 5.91 μm as the calcination temperature was increased up to 1000°C, and the microparticles began to aggregate, with diameters ranging from 20 to 600 nm.

The average size of the primary particles increased from 30 to 390 nm as the calcination temperature was increased up to 1000°C. The HRTEM image shows an enlarged view of the (001) fringes of Li2MnO3 and (003) fringes of LiMO2, where the lattice spacing of 0.47 nm indicates the (001) fringes of Li2MnO3 and (003) fringes of LiMO2 (M = Ni, Co, Mn). It was difficult to distinguish the formation of the Li2MnO3 phase in the HRTEM because lattice fringes of both overlapped. Thus, results of XRD analysis were used to demonstrate the formation of the Li2MnO3 and LiMO2 phases.

Figure 4 shows the effect of calcination temperature on the particle size distribution (PSD) and specific surface area of 0.4Li2MnO3·0.6Li(Mn0.43Ni0.36Co0.21)O2 microparticles. The surface area decreased from 23.9 to 0.59 m2 g⁻¹ as the calcination temperature was increased from 700 to 1000°C; there was a dramatic drop in the surface area at the calcination temperature of 800°C. The mean particle size increased from 1.92 to 3.59 μm when the calcination temperature was increased from 700 to 900°C. The results of PSD analysis were consistent with the morphology characteristics shown in Fig. 3.

XRD patterns of the calcined 0.4Li2MnO3·0.6Li(Mn0.43Ni0.36Co0.21)O2 microparticles are presented in Fig. 5. LiMO2 (M = Ni, Co, Mn) in the microcomposites has a hexagonal α-NaFeO2 structure with a space group of R3m. The degree of ordering in the layered structure of the LiMO2 can be assessed based on the formation of split peaks at 2θ 64–66° corresponding to the (018) and (110) reflections. The splitting of the peak clearly occurred in the microcomposites calcined at temperatures ≥800°C. The composite particles calcined at 700°C also contained split peaks, but the degree of splitting was not distinct. In the XRD pattern of the particles calcined at 600°C, split peaks were not observed.

The structure of Li2MnO3 is similar to that of the LiMO2 with an R3m layered rock-salt structure. However, Li2MnO3 has a monoclinic structure with a space group of C2/m formed by the super-lattice ordering of Li⁺ and Mn⁴⁺, which exists in the transition metal (TM) layer. In addition, the microparticles calcined at temperatures above 700°C exhibit diffraction peaks. However, the peaks of the microparticles calcined at 700°C appear to be highly disordered, given that some peaks are broadened. A disordered peak indicates a high density of stacking disorders, which can cause an increase in the capacity but a rapid decrease in cycle stability. Moreover, the microparticles calcined at 1000°C have secondary Li4Mn5O12 peaks at 38 and 43°, which could be attributed to the evaporation of Li-ions.

Figure 6 shows the initial charge/discharge curves of the calcined 0.4Li2MnO3·0.6Li(Mn0.43Ni0.36Co0.21)O2 microparticles in different temperatures cycled in the voltage range of 2.0–4.6 V at a current density of 0.1 C (where 1 C = 200 mA h g⁻¹). All the initial charge curves have two clearly distinguishable voltage regions. Region A of the curves, exhibiting a plateau at ~4.5 V, corresponds to the oxidation of nickel and cobalt at ~4.5 V and region B corresponds to the irreversible loss of oxygen due to the decomposition reaction by the activation of Li2MnO3 at ~4.5 V. Considering this result, the calcined microparticles at 700°C are desirable, of which temperature is relatively lower than those of other solid-state reaction or liquid-phase methods.

The structure of Li2MnO3 is similar to that of the LiMO2 with an R3m layered rock-salt structure. However, Li2MnO3 has a monoclinic structure with a space group of C2/m formed by the super-lattice ordering of Li⁺ and Mn⁴⁺, which exists in the transition metal (TM) layer. Small satellite peaks located at 2θ 64–66° are indicative of the formation of the Li2MnO3 phase.

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found that an increase in the Li$_2$MnO$_3$ content of the composites resulted in a shift to higher voltage in the initial charge curve and the voltage plateau (at 4.45 V) became longer. Johnson et al. used the I$_{020}$/I$_{003}$ intensity ratio ($C_2/m$ to $R_3m$) as a rough guide for determining the Li$_2$MnO$_3$ content in xLiMnO$_3$·(1−x)LiMO$_2$ composite particles. A shift in the initial charge curve was also observed for our 0.4Li$_2$MnO$_3$·0.6Li(Mn$_{0.43}$Ni$_{0.36}$Co$_{0.21}$)O$_2$ microcomposites. In addition, an increase in the intensity ratio from 0.047 to 0.053 was observed as the calcination temperature was increased. Moreover, the first-cycle coulombic efficiency (CE) decreased from 87 to 80%, as the calcination temperature was increased, as shown in the inserted table in Fig. 6. These results indicate that the Li$_2$MnO$_3$ content in xLiMnO$_3$·(1−x)LiMO$_2$ increased. This is because the irreversible capacity loss on the initial charge and discharge results from electrochemical activation involving Li$_2$O extraction from Li$_2$MnO$_3$. Thus, based on the aforementioned results, we can conclude that an increase in the calcination temperature increases the content of Li$_2$MnO$_3$ in xLiMnO$_3$·(1−x)LiMO$_2$.

The initial discharge capacities of the calcined microparticles decreased with increasing calcination temperature: 251 mA h g$^{-1}$ at 700 and 800°C, 242 mA h g$^{-1}$ at 900°C, and 211 mA h g$^{-1}$ at 1000°C. Although the initial charge and discharge capacities were reported to increase with an increase in the Li$_2$MnO$_3$ content, in this study, the microparticles calcined at 700°C had a low Li$_2$MnO$_3$ content but a high initial discharge capacity of 251 mA h g$^{-1}$. This could be explained by the disordered peak containing a high density of stacking disorders, as shown in Fig. 5. Normally, a material without defects has the lowest energy state; defects in materials increase the energy state. Thus, the composites with defects lowered the activation barrier for Li diffusion and enabled Li to be extracted at a lower potential, which increased the initial capacity.

Moreover, the capacity decreased with an increase in the calcination temperature, although the Li$_2$MnO$_3$ content increased. This was due to an increase in the particle size and a decrease in the surface area. When the particle size increases, lithium diffusion becomes difficult because of the barrier to diffusion for the Li-ions within a cathode particle and the difficulty in electron transport through the bulk of the cathode particle. The capacity of the microparticles calcined at 1000°C largely decreases. This is thought to be due to the formation of Li$_4$Mn$_5$O$_{12}$ by evaporation of the Li-ions at a high calcination temperature (Fig. 5). Thus, in this study, the capacity did not appear to be strongly affected by the increase of Li$_2$MnO$_3$ content in xLiMnO$_3$·(1−x)LiMO$_2$ microparticles, but rather by the morphology, specific surface area, and crystal structure. The microparticles calcined at 800°C were decorated with nanosized grains, and thus had the highest capacity (251 mA h g$^{-1}$).

To investigate the effect of calcination temperature on the rate capability of 0.4Li$_2$MnO$_3$·0.6Li(Mn$_{0.43}$Ni$_{0.36}$Co$_{0.21}$)O$_2$, the calcined microparticles were galvanostatically charged at a current density of 0.1 C before each discharging test, and then the current density was changed from 0.1 to 2 C. Figure 7 shows the rate capability of the microparticles cycled over a voltage range of 2.0–4.6 V. The specific surface areas of the microparticles decreased with increasing the calcination temperature (Fig. 4). The rate capability is related to the specific surface area and primary particle size of the microparticles. Increase in the surface area and decrease in primary particle size accelerate the diffusion of Li ions in the composite particles—due to their short diffusion pathway—which improves the rate capability. Thus, the spherical microparticles with nanosized grains and pure well-crystallized phase (calcined at 800°C) showed a good rate performance. However, the capacity of the microparticles calcined at 700°C showed a high initial discharge capacity; the capacity decreased sharply as the current density increased, which can be explained based on the XRD and BET analyses. The microparticles had high capacity due to the disordered peak and high surface area (mentioned above), did not have a well-ordered layered structure.
of LiMO₂, and had crystal defects in Li₂MnO₃. These factors can result in an unstable cycle property, especially for a high cut-off voltage and high current density. Moreover, the microparticles calcined at 1000°C showed a rapid decrease in capacity at the high current density of 2 C, which was attributed to the large grain size and low surface area (0.59 m² g⁻¹). To sum up, the rate capability was maximized with a sample calcined at 800°C although the sample calcined at 800°C had lower surface area than that of the samples at 700°C. It was because the sample had not only optimal point in primary grain size and specific surface, but also well-developed crystal structures.

Figure 8 shows the capacity retention of 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles over the voltage range of 2.0–4.6 V at 25°C and a current density of 0.5 C. Testing was done after the rate capability test. Thus, the capacity retention ratio was calculated using the equation shown in Fig. 8. All the composite particles showed a stable charge/discharge capacity after 16 cycles at 25°C, except the microparticles calcined at 700°C. The microparticles calcined at 700°C retained 83% of their initial capacity after 16 cycles, which resulted from the unstable structure and high surface area, as shown in Figs. 3 and 4. The high surface area of cathode materials could, to some degree, help in improving the rate capability, but has negative side effects such as side reactions with electrolyte or dissolutions of transition metal, which finally degrade cycle performance.³³,³⁶,³⁷

Conversely, the microparticles calcined at 800 and 900°C delivered a reasonably steady capacity and retention ratio, as shown in the table inserted in Fig. 8. This occurred because the primary particle size was large enough to minimize side-reactions with the electrolyte, the formation of Li₂MnO₃ (which served as a stabilizer), and the well-developed layered structure of LiMO₂. The slight difference in capacity could be attributed to the difference in surface area. The microparticles calcined at 1000°C had excellent cycling performance (97% after 16 cycles), but considerably lower capacity due to the increase in the diffusion pathway caused by the large particle size and secondary phase.

4. Conclusions

Spherical 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂ microparticles with nanosized grains were successfully prepared by a two-step process: spray pyrolysis followed by low-temperature calcination. The microstructure and crystal structure were strongly dependent on the calcination temperature, which affected the electrochemical performance. The good rate capability and cycle stability of the microparticles calcined at 800°C were ascribed to the following factors: (1) the formation of a well-developed Li₃MnO₃ phase, which supplies surplus Li-ions to the LiMO₂ component as a stabilizer; (2) appropriate particle size and specific surface area, which minimize electrolyte-induced side reactions; and (3) a well-developed hexagonal α-NaFeO₂ structure. Spray pyrolysis was shown to be effective for preparing the layered cathode materials LiₓMnO₂ (x = 0.4Li₂MnO₃·0.6Li(Mn₀.₄₃Ni₀.₃₆Co₀.₂₁)O₂). Compared to other processes, spray pyrolysis can be used to prepare composite particles at low calcination temperatures while allowing for the existence of nanosized grains, which can improve electrical performance.

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References

1) L. Ji, P. Meduri, V. Agubra, X. Xiao and M. Alcoutlabi, Adv. Energy Mater., 6, 1502159–1502232 (2016).
2) A. Andersson, D. Abraham, R. Haaseh, S. MacLaren, J. Liu and K. Amine, J. Electrochem. Soc., 149, A1358–A1369 (2002).
3) J.-M. Tarascon and M. Armand, Nature, 414, 359–367 (2001).
4) J. Liu, S. Wang, Z. Ding, R. Zhou, Q. Xia, J. Zhang, L. Chen, W. Wei and P. Wang, ACS Appl. Mater. Interfaces, 8, 18008–18017 (2016).
5) E. C. Evarts, Nature, 526, 593–595 (2015).
6) B. L. Ellis, K. T. Lee and L. F. Nazar, Chem. Mater., 22, 691–714 (2010).
7) M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek and S. Hackney, J. Mater. Chem., 17, 3112–3125 (2007).
8) J.-S. Kim, C. Johnson, J. Vaughey and M. Thackeray, J. Power Sources, 153, 258–264 (2006).
9) A. Abouimrane, Y. Cui, Z. Chen, I. Belharouak, H. B. Yahia, H. Wu, R. Assary, L. A. Curtiss and K. Amine, Nano Energy, 27, 196–201 (2016).
10) S.-H. Kang, Y. Sun and K. Amine, Electrochem. Solid-State Lett., 6, A183–A186 (2003).
11) M. N. Ates, S. Mukerjee and K. Abraham, J. Electrochem. Soc., 161, A355–A363 (2014).
12) A. R. Armstrong and P. G. Bruce, Nature, 381, 499–500 (1996).
13) M. S. Whittingham, Chem. Rev., 104, 4271–4302 (2004).
14) J. Liu, Q. Wang, B. Rejea-Jayan and A. Manthiram, Electrochem. Commun., 12, 750–753 (2010).
15) D. Luo, G. Li, C. Fu, J. Zheng, J. Fan, Q. Li and L. Li, Adv. Energy Mater., 4, 1400062 (2014).
16) J. Liu and A. Manthiram, J. Mater. Chem., 20, 3961–3967 (2010).
17) S.-H. Kang and M. M. Thackeray, Electrochem. Commun., 11, 748–751 (2009).
18) R. Santhanam and B. Ramabubu, J. Power Sources, 195, 4313–4317 (2010).
19) J.-H. Lim, H. Bang, K.-S. Lee, K. Amine and Y.-K. Sun, J. Power Sources, 189, 571–575 (2009).
20) D. Kim, J. Gim, J. Lim, S. Park and J. Kim, Mater. Res. Bull., 45, 252–255 (2010).
21) M. Konarova and I. Taniguchi, J. Power Sources, 195, 3661–3667 (2010).
22) S. Park, S.-W. Oh, S. Kang, I. Belharouak, K. Amine and Y.-K. Sun, *Electrochim. Acta*, 52, 7226–7230 (2007).
23) D. S. Jung, S. B. Park and Y. C. Kang, *Korean J. Chem. Eng.*, 27, 1621–1645 (2010).
24) J. Y. Seo, K. Lee, S. Y. Lee, S. G. Jeon, J.-G. Na, Y.-K. Oh and S. B. Park, *Bioresour. Technol.*, 152, 562–566 (2014).
25) J. Y. Seo, H. W. Kang, D. S. Jung, H. M. Lee and S. B. Park, *Mater. Res. Bull.*, 48, 1484–1489 (2013).
26) C.-C. Wang, K. A. Jarvis, P. J. Ferreira and A. Manthiram, *Chem. Mater.*, 25, 3267–3275 (2013).
27) J. R. Croy, K. G. Gallagher, M. Balasubramanian, Z. Chen, Y. Ren, D. Kim, S.-H. Kang, D. W. Dees and M. M. Thackeray, *J. Phys. Chem. C*, 117, 6525–6536 (2013).
28) S.-H. Kang, C. Johnson, J. Vaughey, K. Amine and M. Thackeray, *J. Electrochem. Soc.*, 153, A1186–A1192 (2006).
29) M. Kotobuki, M. Koishi and Y. Kato, *Ionics*, 19, 1945–1948 (2013).
30) C. Wan, Y. Nuli, Q. Wu, M. Yan and Z. Jiang, *J. Appl. Electrochem.*, 33, 107–112 (2003).
31) M. Hou, S. Guo, J. Liu, J. Yang, Y. Wang, C. Wang and Y. Xia, *J. Power Sources*, 287, 370–376 (2015).
32) C. S. Johnson, N. Li, C. Lefief, J. T. Vaughey and M. M. Thackeray, *Chem. Mater.*, 20, 6095–6106 (2008).
33) M.-S. Park, J.-W. Lee, W. Choi, D. Im, S.-G. Doo and K.-S. Park, *J. Mater. Chem.*, 20, 7208–7213 (2010).
34) B. Kang and G. Ceder, *Nature*, 458, 190–193 (2009).
35) T. Drezen, N.-H. Kwon, P. Bowen, I. Teerlinck, M. Isono and I. Exnar, *J. Power Sources*, 174, 949–953 (2007).
36) J. H. Kim, S. H. Choi, M. Y. Son, M. H. Kim, J.-K. Lee and Y. C. Kang, *Ceram. Int.*, 39, 331–336 (2013).
37) Y. Wu and A. Manthiram, *Solid State Ionics*, 180, 50–56 (2009).