

Cite this: *RSC Adv.*, 2014, 4, 44203

# Characteristics of precursor powders of a nickel-rich cathode material prepared by a spray drying process using water-soluble metal salts†

Gi Dae Park and Yun Chan Kang\*

The electrochemical properties of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  as a cathode material prepared by a simple spray drying process are investigated. Citric acid, which is used as the chelating agent, enables the production of the lithium-containing precursor powders with uniform compositions from the water-soluble metal salts by a spray drying process. The post-treatment of the precursor powders under an atmosphere of oxygen results in a cathode material in the form of a powder with good electrochemical properties. The composition of the powders is determined by inductively coupled plasma analysis to be  $\text{Li}_{1.05}\text{Ni}_{0.81}\text{Co}_{0.15}\text{Al}_{0.04}\text{O}_2$ . The discharge capacities of the powders post-treated at 750 °C after the 1<sup>st</sup> and 100<sup>th</sup> cycles are 188 and 178 mA h g<sup>-1</sup>, respectively. The simple spray drying process is successfully applied to the preparation of precursors of the cathode material with complex compositions. The electrochemical properties of the micron sized  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  aggregates with a filled morphology prepared from the precursor powders obtained by the spray drying process are also investigated. The aggregated powders obtained by the second spray drying process show a discharge capacity of 161 mA h g<sup>-1</sup> after 100 cycles.

Received 12th August 2014  
Accepted 5th September 2014

DOI: 10.1039/c4ra08524h

[www.rsc.org/advances](http://www.rsc.org/advances)

## Introduction

Partial substitution of nickel in the layered  $\text{LiNiO}_2$  system by transition or non-transition metals has been reported to improve their electrochemical properties as cathode materials for lithium ion batteries (LIBs).<sup>1–32</sup>  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  has specifically been considered as a promising cathode material among other Ni-rich candidates because of its improved stability and electrochemical performance caused by substitution of Ni by Co and Al in  $\text{LiNiO}_2$ .<sup>12–26</sup>

The electrochemical performance of cathode materials is strongly affected by the morphology, mean size, and the phase homogeneity of the powders.<sup>21–32</sup> Micron sized spherical powders have been mainly applied as cathode materials in LIBs because of their high tap density and volumetric energy density.<sup>26–32</sup> To improve the phase homogeneity of the cathode powders, various types of solution and gas phase reaction methods have been used in the preparation of the precursor powders. Coprecipitation, which is one of the important solution methods used in the preparation of the precursor powders, is disadvantageous in terms of exercising precise control of the composition of the lithium-free precursor powders because the precipitation conditions of metal ions

are strongly affected by the metal components. Taniguchi *et al.* prepared phase homogeneous precursor powders containing lithium with various compositions by ultrasonic spray pyrolysis, which is a gas phase reaction method.<sup>33–35</sup> The micron sized precursor powders obtained by ultrasonic spray pyrolysis were processed by high-energy milling to obtain the colloidal spray solution for spray drying. The micron sized spray dried powders with filled morphology showed good electrochemical properties after post-treatment at temperatures above 400 °C.

Spray drying is advantageous in the large-scale production of precursor powders with complex compositions.<sup>36–42</sup> However, the preparation of precursor powders by spray drying using water soluble precursor salts has scarcely been studied.<sup>40–42</sup> Water-soluble metal salts are difficult to spray dry because they produce highly hygroscopic powders, which are prone to become sticky. In this study, the possibility of using spray drying for producing precursor powders for the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathode material was investigated. Citric acid enabled the production of precursor powders containing lithium with uniform compositions from the water-soluble metal salts. The electrochemical properties of the post-treated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders obtained from the spray dried precursor powders were investigated. In addition, micron sized  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  aggregates with filled morphologies were prepared by a two-step spray drying process.

Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea. E-mail: yckang@korea.ac.kr

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra08524h

## Experimental

A commercial spray drying process was used to prepare the precursor powders with a hollow structure. The temperatures at the inlet and outlet of the spray dryer were set to 350 °C and 150 °C, respectively. A two-fluid nozzle was used as an atomizer and the atomization pressure was set to 0.3 bar. The precursor solution was prepared by dissolving nickel nitrate hexahydrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , Aldrich], cobalt nitrate hexahydrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , Aldrich], and aluminum nitrate nonahydrate  $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ , Aldrich] in distilled water. The lithium content added to the spray solution was 20% higher than the stoichiometric amount required to obtain  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ . The overall concentration of nickel, cobalt, and aluminum was 0.5 M. The concentration of citric acid used as a chelating agent was 0.3 M. The precursor particles obtained by spray drying were post-treated at temperatures ranging from 300 and 800 °C for 3 h under oxygen atmosphere. The precursor powders post-treated at 700 °C were wet-milled using a planetary mill to obtain the colloidal spray solution for the second step of spray drying. The powders spray dried in the second step were post-treated at 750 °C for 3 h under an oxygen atmosphere.

X-ray diffraction (XRD) patterns of the prepared cathode powders were obtained using a Rigaku DMAX-33 diffractometer at the Korea Basic Science Institute (Daegu). The morphological characteristics of the samples were investigated using a scanning electron microscope (SEM, JEOL JSM-6060) and by high-resolution transmission electron microscopy (TEM, JEOL JEM-2010). The decomposition characteristics of the precursor powders were determined by using TGA (Perkin Elmer Pyris 1) and DSC (Perkin Elmer DSC8000), which were performed in air at a heating rate of 10 °C min<sup>-1</sup>. The specific surface areas of the powders were calculated by Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption measurements (TriStar 3000).

The initial charge–discharge capacities and cycle properties of the prepared  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders were measured using 2032-type coin cells. The cathode was composed of 80 wt% of the active material, 10 wt% of teflonized acetylene black, and 10 wt% of the binder with a few drops of alcohol. Lithium and a polypropylene film were used as the anode and the separator, respectively. Lithium hexafluorophosphate (1 M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1 : 1 volume ratio was used as the electrolyte. The charge–discharge characteristics of the samples were measured by cycling in the potential range 2.8–4.5 V.

## Results and discussion

The morphologies of the precursor powders containing Li, Ni, Co, and Al prepared by spray drying from the spray solution containing citric acid are shown in Fig. 1. The powders were spherical and hollow and showed a thin wall structure. Necking between particles did not occur because of the low hygroscopicity of the dried powders. The high drying rate of the droplet and gas evolution during drying resulted in precursor powders with hollow structures. The chelate complex formed by the chelation of Li, Ni, Co, and Al ions with citric acid could be

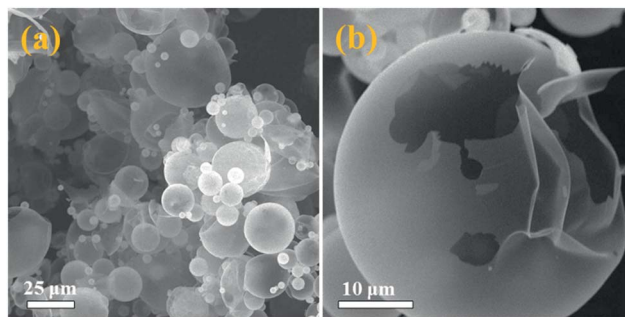


Fig. 1 Morphologies of the precursor powders directly prepared by spray drying process from the spray solution with citric acid.

recovered easily in the spray drying system. On the other hand, the dried powders obtained from the spray solution without citric acid could not be recovered in the spray drier because of their high hygroscopicity.

The TG curve of the powders directly obtained by spray drying process is shown in Fig. 2. The TG curve showed three distinct weight losses at temperatures below 360 °C. The first weight loss caused by the evaporation of adsorbed water molecules occurred at temperatures below 200 °C. The decomposition of the metal chelates occurred in two steps between 200 and 330 °C. The strong exothermic peak observed at 329 °C in the DSC curve reveals the decomposition of the metal chelate. The total weight loss caused by the evaporation of adsorbed water molecules and decomposition of metal chelates was 70.7%.

The XRD patterns of the powders post-treated at various temperatures are shown in Fig. 3. The powders post-treated at 300 °C showed the main peaks of Ni and minor peaks of CoO and Li<sub>2</sub>O. Decomposition of the metal chelates resulted in a reductive atmosphere caused by the evolution of CO gas. Therefore, powders with oxygen-poor phases of Ni and Co components were formed at a low post-treatment temperature of 300 °C. The powders post-treated at 500 °C showed the main peaks of NiO and low intensity peaks of Li<sub>2</sub>O. The peaks related

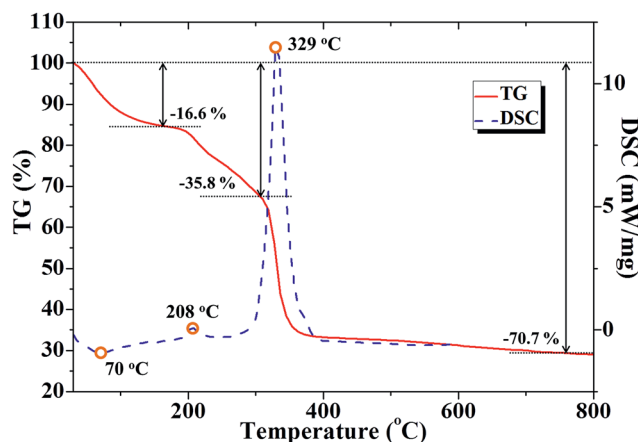


Fig. 2 TG/DSC curves of the precursor powders directly prepared by spray drying process from the spray solution with citric acid.

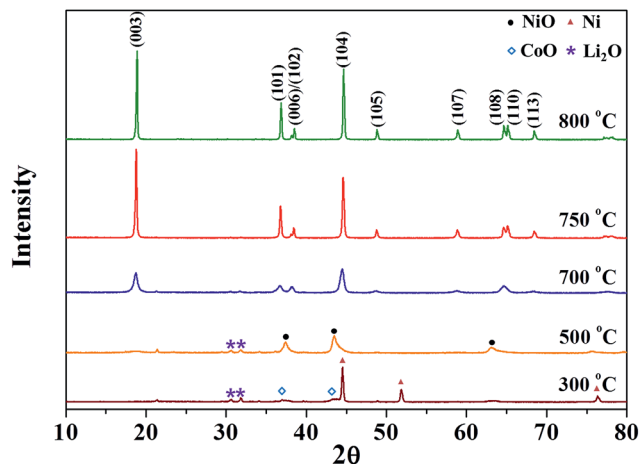


Fig. 3 XRD patterns of the powders post-treated at temperatures between 300 and 800 °C.

to Co were not observed in the XRD pattern of the powders post-treated at 500 °C. It is well known that the NiO–CoO solid solution can easily be formed. Therefore, the Co component formed the NiO–CoO solid solution at a post-treatment temperature of 500 °C. The reaction of the Li component with Ni and Co components occurred at a post-treatment temperature of 700 °C. However, the separation of the 108/110 peaks in the XRD patterns, which indicate an ordered distribution of Li and Ni–Co–Al in a layered structure and good electrochemical properties, occurred in the samples post-treated at 750 °C and 800 °C.<sup>26</sup> The mean crystallite sizes of the powders post-treated at 750 °C and 800 °C were 44 and 51 nm, respectively. The compositions of the powders before and after post-treatment at 750 °C, as determined by ICP-OES analysis, are shown in Table 1. The composition of the powders was found to be  $\text{Li}_{1.05}\text{Ni}_{0.81}\text{Co}_{0.15}\text{Al}_{0.04}\text{O}_2$ . The composition of the precursor powders was well maintained even after post-treatment.

The morphologies of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at various temperatures are shown in Fig. 4. The powders post-treated at 700 °C showed the spherical shape of the precursor powders directly prepared by spray drying. The powders aggregated at post-treatment temperatures of 750 °C and 800 °C. The inset images shown in Fig. 4 show the SEM images of the crushed  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders. The  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at various temperatures were milled by hand using an agate mortar. The powders

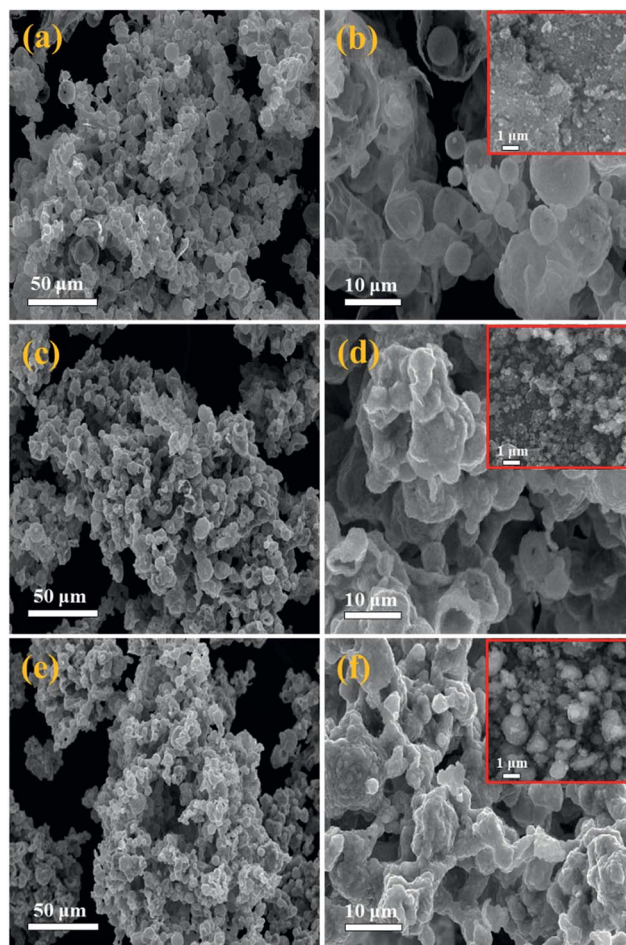


Fig. 4 Morphologies of the powders post-treated at various temperatures: (a) and (b) 700 °C, (c) and (d) 750 °C, (e) and (f) 800 °C.

post-treated at 700 °C and 750 °C were transformed into ultra-fine powders even after simple crushing process by hand. On the other hand, the powders post-treated at 800 °C were large

Table 1 The compositions of the powders before and after post-treatment at 750 °C

Sample	Composition of Ni : Co : Al (atomic ratio)			Composition of Li : $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}$ (atomic ratio)	
	Ni	Co	Al	Li	$\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}$
Precursor	0.809	0.147	0.043	1.056	1
Post-treated at 750 °C	0.806	0.147	0.047	1.051	1

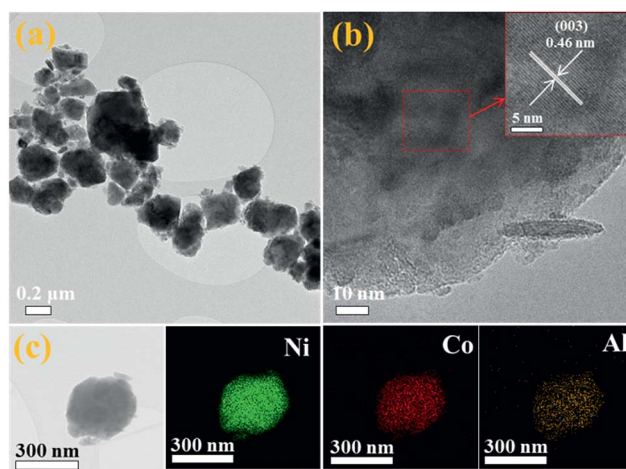


Fig. 5 Morphologies and elemental mapping images of the powders post-treated at 750 °C: (a) low resolution TEM image, (b) high resolution TEM image, and (c) elemental mapping images.



even after crushing. Fig. 5 shows the TEM and dot-mapping images of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at 750 °C after the crushing process. The powders were several hundred nanometers in size and were non-aggregated. The high-resolution TEM image, shown in Fig. 5b, indicates the clear lattice fringes separated by a lattice spacing of 0.46 nm. This lattice spacing value corresponds to the (003) plane of the layered structure. The elemental mapping images shown in Fig. 5c indicate the uniform distribution of Ni, Co, and Al components throughout the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder. The formation of metal chelates minimized the phase separation of each component inside the powder during the simple spray drying process.

Fig. S1† shows the SEM images of the aggregated powders formed by the second spray drying process. The precursor powders shown in Fig. 4a and b were wet-milled in a planetary mill to obtain the colloidal spray solution for the second step of spray drying. The aggregated powders obtained directly by the second spray drying process were spherical and the micron sized powders were non-aggregated. The spherical morphology of the aggregated powders was maintained even after post-treatment at 750 °C for 3 h under an oxygen atmosphere. However, the grain size of the aggregated powders increased after post-treatment, as shown in Fig. S1b and d.† The mean size of the aggregated powders after post-treatment at 750 °C was 3.0  $\mu\text{m}$ . The  $\text{N}_2$  adsorption and desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distributions of the aggregated powders formed by the second step spray drying process are shown in Fig. S2.† The aggregated powders obtained before post-treatment had well-developed mesopores. However, the aggregated powders obtained after post-treatment at 750 °C had dense structure without pores. The BET surface areas of the aggregated powders formed by the second spray drying process before and after post-treatment were 13.6 and 0.7  $\text{m}^2 \text{g}^{-1}$ , respectively.

Fig. 6 shows the initial charge and discharge curves of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at various temperatures tested at 25 °C under a constant current density of 100  $\text{mA g}^{-1}$ .

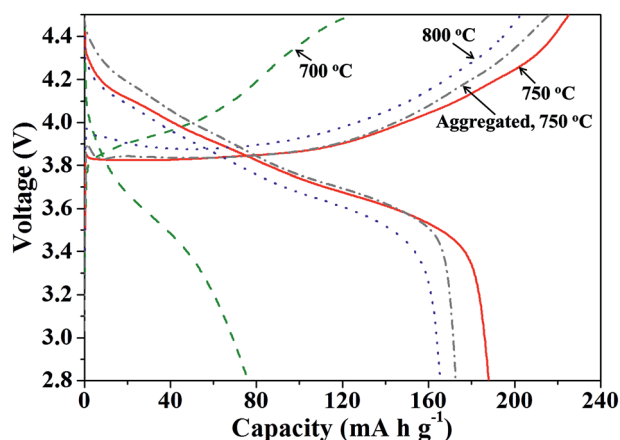


Fig. 6 Initial charge and discharge curves of the powders post-treated at various temperatures and aggregated powders.

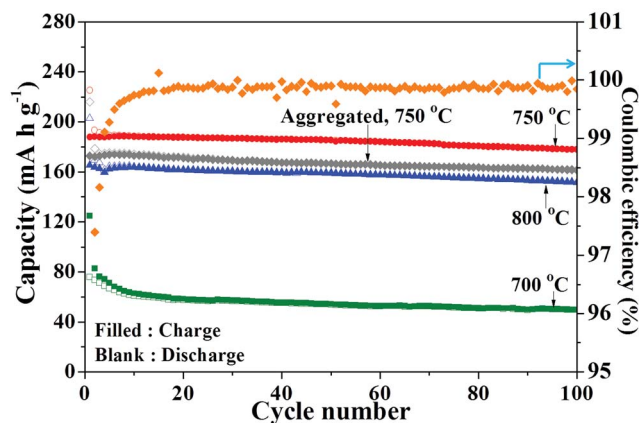


Fig. 7 Cycling performances of the powders post-treated at various temperatures and aggregated powders.

The powders post-treated at a low temperature of 700 °C showed low initial charge and discharge capacities. The ultrafine powders with an ordered distribution of Li and Ni-Co-Al in the layered structure post-treated at 750 °C showed the maximum initial charge and discharge capacities of 225 and 188  $\text{mA h g}^{-1}$ , respectively. The aggregated powders obtained by the two-step spray drying process showed initial charge and discharge capacities of 216 and 173  $\text{mA h g}^{-1}$  after post-treatment at 750 °C, respectively. The aggregated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders showed lower capacities than the nanopowders post-treated at 750 °C. However, the capacities of the aggregated powders could be improved by optimizing the preparation conditions, such as the post-treatment temperature of the precursor powders and milling conditions used for the preparation of the spray solution used for the second spray drying. The high-energy wet milling may induce the formation of lithium deficient  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders.

The cycling performances of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at various temperatures at a constant current density of 100  $\text{mA g}^{-1}$  are shown in Fig. 7. The  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at 750 °C and 800 °C showed better cycling performances than powders post-treated at 700 °C. The discharge capacities of the powders post-treated at 700 °C, 750 °C, and 800 °C after 100 cycles were 50, 178, and 151  $\text{mA h g}^{-1}$ , respectively. The Coulombic efficiencies of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powders post-treated at 750 °C reached to 99% after 4 cycles and the values were maintained during the subsequent cycles. Therefore, the spray drying process could be successfully applied to the preparation of precursors for cathode materials with complex compositions. The aggregated powders obtained by the two-step spray drying process showed a discharge capacity of 161  $\text{mA h g}^{-1}$  after 100 cycles.

## Conclusions

The possibility of using spray drying for the large-scale production of precursor powders of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathode material was investigated. The hollow precursor

powders containing Li, Ni, Co, and Al components were successfully prepared by spray drying. The precursor powders prepared from the spray solution containing citric acid as the chelating agent were stable under spray drying conditions of high humidity. The  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  nanopowders formed by the post-treatment of the precursor powders obtained by the spray drying process showed high initial charge and discharge capacities and good cycling performances. Therefore, the simple spray drying process was appropriate to produce the precursor powders for cathode materials with complex compositions. The precursor powders with thin-walled hollow structures directly prepared by the spray drying process could be used in a large-scale second step spray drying process to produce micron sized powders with spherical shape and dense structure, which can be used as a cathode material for LIBs.

## Acknowledgements

"This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (no. 2012R1A2A2A02046367)."

## Notes and references

- 1 Y. H. Cho, P. G. Oh and J. P. Cho, *Nano Lett.*, 2013, **13**, 1145.
- 2 M. Lengyel, X. Zhang, G. Atlas, H. L. Bretscher, I. Belharouak and R. L. Axelbaum, *J. Electrochem. Soc.*, 2014, **161**, A1338.
- 3 T. Kobayashi, Y. Kobayashi, M. Tabuchi, K. Shono, Y. Ohno, Y. Mita and H. Miyashiro, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12387.
- 4 M. Q. Xu, N. Tsiouvaras, A. Garsuch, H. A. Gasteiger and B. L. Lucht, *J. Phys. Chem. C*, 2014, **118**, 7363.
- 5 M. Shui, S. Gao, J. Sun, W. Zheng, D. Xu, L. Chen, L. Feng and Y. Ren, *Ionics*, 2013, **19**, 41.
- 6 M. Bettge, Y. Li, B. Sankaran, N. D. Rago, T. Spila, R. T. Haasch, I. Petrov and D. P. Abraham, *J. Power Sources*, 2013, **233**, 346.
- 7 X. F. Bie, F. Du, Y. Wang, K. Zhu, H. Ehrenberg, K. Nikolowski, C. Z. Wang, G. Chen and Y. J. Wei, *Electrochim. Acta*, 2013, **97**, 357.
- 8 S. K. Jung, H. J. Gwon, J. H. Hong, K. Y. Park, D. H. Seo, H. G. Kim, J. S. Hyun, W. Y. Yang and K. S. Kang, *Adv. Energy Mater.*, 2014, **4**, 1300787.
- 9 D. P. Abraham, R. D. Twisten, M. Balasubramanian, J. Kropf, D. Fischer, J. McBreen, I. Petrov and K. Amine, *J. Electrochem. Soc.*, 2003, **150**, A1450.
- 10 J. H. Shim, S. H. Lee and S. S. Park, *Chem. Mater.*, 2014, **26**, 2537.
- 11 Y. M. Song, J. G. Han, S. J. Park, K. T. Lee and N. S. Choi, *J. Mater. Chem. A*, 2014, **2**, 9506.
- 12 S. Y. Hwang, W. Y. Chang, S. M. Kim, D. Su, D. H. Kim, J. Y. Lee, K. Y. Chung and E. A. Stach, *Chem. Mater.*, 2014, **26**, 1084.
- 13 C. J. Han, J. H. Yoon, W. I. Cho and H. Jang, *J. Power Sources*, 2004, **136**, 132.
- 14 C. H. Chen, J. Liu, M. E. Stoll, G. Henriksen, D. R. Vissers and K. Amine, *J. Power Sources*, 2004, **128**, 278.
- 15 D. P. Abraham, S. Kawauchi and D. W. Dees, *Electrochim. Acta*, 2008, **53**, 2121.
- 16 I. Belharouak, W. Lu, D. Vissers and K. Amine, *Electrochem. Commun.*, 2006, **8**, 329.
- 17 W. S. Yoon, K. Y. Chung, J. McBreen and X. Q. Yang, *Electrochem. Commun.*, 2006, **8**, 1257.
- 18 H. Yang and J. Prakash, *J. Electrochem. Soc.*, 2004, **151**, A1222.
- 19 C. Täubert, M. Fleischhammer, M. W. Mehrens, U. Wietelmann and T. Buhrmester, *J. Electrochem. Soc.*, 2010, **157**, A721.
- 20 I. Belharouak, D. Vissers and K. Amine, *J. Electrochem. Soc.*, 2006, **153**, A2030.
- 21 S. H. Ju, J. H. Kim and Y. C. Kang, *Met. Mater. Int.*, 2010, **16**, 299.
- 22 S. H. Lee, C. S. Yoon, K. Amine and Y. K. Sun, *J. Power Sources*, 2013, **234**, 201.
- 23 Y. H. Cho and J. P. Cho, *J. Electrochem. Soc.*, 2010, **157**, A625.
- 24 Y. M. Chung, S. H. Ryu, J. H. Ju, Y. R. Bak, M. J. Hwang, K. W. Kim, K. K. Cho and K. S. Ryu, *Bull. Korean Chem. Soc.*, 2010, **31**, 2304.
- 25 M. K. Jo, M. J. Noh, P. G. Oh, Y. S. Kim and J. P. Cho, *Adv. Energy Mater.*, 2014, **4**, DOI: 10.1002/aenm.201301583.
- 26 S. H. Ju, H. C. Jang and Y. C. Kang, *Electrochim. Acta*, 2007, **52**, 7286.
- 27 Y. K. Sun, D. J. Lee, Y. J. Lee, Z. Chen and S. T. Myung, *ACS Appl. Mater. Interfaces*, 2013, **5**, 11434.
- 28 S. H. Ju and Y. C. Kang, *J. Power Sources*, 2008, **178**, 387.
- 29 G. Zou, X. K. Yang, X. Y. Wang, L. Ge, H. B. Shu, Y. S. Bai, C. Wu, H. P. Guo, L. Hu, X. Yi, B. Ju, H. Hu, D. Wang and R. Yu, *J. Solid State Electrochem.*, 2014, **18**, 1789.
- 30 S. H. Ju and Y. C. Kang, *Mater. Chem. Phys.*, 2008, **107**, 328.
- 31 S. H. Ju and Y. C. Kang, *Electrochim. Acta*, 2010, **55**, 6088.
- 32 S. H. Ju and Y. C. Kang, *Ceram. Int.*, 2009, **35**, 1205.
- 33 Z. Bakenov and I. Taniguchi, *J. Electrochem. Soc.*, 2010, **157**, A430.
- 34 T. N. L. Doan, Z. Bakenov and I. Taniguchi, *Adv. Powder Technol.*, 2010, **21**, 187.
- 35 I. Taniguchi, N. Fukuda and M. Konarova, *Powder Technol.*, 2008, **181**, 228.
- 36 D. S. Jung, T. H. Hwang, S. B. Park and J. W. Choi, *Nano Lett.*, 2013, **13**, 2092.
- 37 M. Li, X. Hou, Y. Sha, J. Wang, S. Hu, X. Liu and Z. P. Shao, *J. Power Sources*, 2014, **248**, 721.
- 38 Y. J. Lv, Y. F. Long, J. Su, X. Y. Lv and Y. X. Wen, *Electrochim. Acta*, 2014, **119**, 155.
- 39 D. S. Wang, M. X. Gao, H. G. Pan, Y. F. Liu, J. H. Wang, S. Q. Li and H. W. Ge, *J. Alloys Compd.*, 2014, **604**, 130.
- 40 S. H. Choi and Y. C. Kang, *Chem. - Eur. J.*, 2014, **20**, 5835.
- 41 M. Y. Son, J. H. Kim and Y. C. Kang, *Electrochim. Acta*, 2014, **116**, 44.
- 42 J. H. Kim, Y. S. Jang, B. K. Park and Y. C. Kang, *Int. J. Electrochem. Sci.*, 2013, **8**, 1067.