

Aalborg Universitet

Green and low-cost synthesis of LiNi_{0.8}Co_{0.15}Al_{0.05}O2 cathode material for Li-ion batteries

Liu, Wanmin; Qin, M.L.; Gao, Chengwei; Yu, Donghong; Yue, Yuanzheng

Published in: **Materials Letters**

DOI (link to publication from Publisher): 10.1016/j.matlet.2019.03.064

Creative Commons License CC BY-NC-ND 4.0

Publication date: 2019

Document Version Accepted author manuscript, peer reviewed version

Link to publication from Aalborg University

Citation for published version (APA):

Liu, W., Qin, M. L., Gao, C., Yu, D., & Yue, Y. (2019). Green and low-cost synthesis of LiNi Co Al O2 cathode material for Li-ion batteries. *Materials Letters*, *246*, 153-156. https://doi.org/10.1016/j.matlet.2019.03.064

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
 You may not further distribute the material or use it for any profit-making activity or commercial gain
 You may freely distribute the URL identifying the publication in the public portal -

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from vbn.aau.dk on: December 04, 2025

Accepted Manuscript

Green and low-cost synthesis of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material for Liion batteries

Wanmin Liu, Mulan Qin, Chengwei Gao, Donghong Yu, Yuanzheng Yue

PII: S0167-577X(19)30453-7

DOI: https://doi.org/10.1016/j.matlet.2019.03.064

Reference: MLBLUE 25902

To appear in: *Materials Letters*

Received Date: 6 January 2019 Revised Date: 12 March 2019 Accepted Date: 18 March 2019



Please cite this article as: W. Liu, M. Qin, C. Gao, D. Yu, Y. Yue, Green and low-cost synthesis of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode material for Li-ion batteries, *Materials Letters* (2019), doi: https://doi.org/10.1016/j.matlet.2019.03.064

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Green and low-cost synthesis of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode material for Li-ion

batteries

Wanmin Liu a, b*, Mulan Qin a, Chengwei Gao b, Donghong Yu b, Yuanzheng Yue b

^a Hunan Provincial Key Laboratory of Environmental Catalysis & Waste Recycling, College of

Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

^b Department of Chemistry and Bioscience, Aalborg University, 9220 Aalborg, Denmark

Abstract

A spherical LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) cathode material is synthesized from the

precursor Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ obtained through a co-precipitation method using

potassium sodium tartrate for the first time as a chelating agent. X-ray diffraction

analysis proves that the as-prepared NCA is a hexagonal phase with perfectly ordered

layered structure. Scanning electron microscope study shows that the morphology and

size of NCA remain nearly the same as those of the precursor. Clear crystal lattice

fringes arranged along the (003) plane can be found in transmission electron

microscope images. The NCA material exhibits excellent electrochemical properties

with initial charge/discharge capacities of 245.6/204.4, 201.2/196.3, 189.0/182.2 and

177.3/171.4 mAh·g⁻¹ at 0.1, 0.2, 0.5 and 1.0 C, respectively, and charge/discharge

capacity retentions of 91.9%/91.5% after 100 cycles at 0.5 C in the voltage range of

2.8-4.3 V (vs. Li/Li⁺).

Keywords: Energy storage and conversion; Functional; Nickel-rich lithium cobalt

oxide; Potassium sodium tartrate; Green synthesis

* Corresponding author. Tel./fax: +86 731 58680125.

E-mail addresses: william@hnie.edu.cn; yy@bio.aau.dk

1

1. Introduction

Owing to the advantages in gravimetric capacity, rate capability and capital cost, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) has found relatively widespread commercial applications as a cathode material, for instance, in Panasonic batteries for Tesla electric vehicles [1-3]. To further enhance the electrochemical properties of NCA, various strategies have been proposed. Especially, lots of synthetic methods, such as spray drying [4], cation exchange [5], spray pyrolysis [6], sol-gel [7], solution combustion [8] and coprecipitation [9-14] have been used to prepare NCA with improved electrochemical properties. Among all of the above-mentioned methods, co-precipitation has been generally recognized as the best industrialization method due to its absolute merits with respect to homogenous elemental distribution, well-controlled spherical morphology, good fluidity and high tap density. In a typical co-precipitation route, a mixed sulphate solution of Ni²⁺, Co²⁺ and Al³⁺, NaOH solution and NH₃·H₂O solution acted as the metal ions source, the precipitant and the chelating agent, respectively. Considering the environmental pollution caused by ammonia, 5-sulfosalicylic acid [11] and ethylenediaminetetraacetic acid (EDTA) [12] was explored as the complexing agents to synthesize NCA. However, the utilization of such expensive chelating agents is unfavorable for the industrialization of NCA. Therefore, a cheap and green complexing agent should be developed to prepare NCA.

Potassium sodium tartrate tetrahydrate (C₄H₄O₆KNa·4H₂O) is usually applied in the fields of plating and electroless plating based on its low cost and strong complexing ability with different metal ions including Al³⁺, Ni²⁺ and Co²⁺. Thus, in this work, C₄O₆H₄KNa·4H₂O was firstly used as a chelating agent to synthesize the spherical Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂. Moreover, NCA prepared from this precursor was characterized by the physical and electrochemical methods.

2. Experimental

Stoichiometric amounts of NiSO₄·6H₂O, CoSO₄·7H₂O and Al₂(SO₄)₃·18H₂O were dissolved in deionized water with a molar ratio of 0.8:0.15:0.05 for Ni²⁺:Co²⁺:Al³⁺. Then C₄H₄O₆KNa·4H₂O was dissolved in a 1 mol·L⁻¹ aqueous solution of metal sulphates. The mixed solution and 3 mol·L⁻¹ NaOH solution were simultaneously pumped into a continuous stirred tank reactor. The pH value, temperature, stirring speed and velocity of flow were strictly controlled. After the reaction for 12 h, the precipitate was thoroughly washed with deionized water and then dried at 100 °C for 15 h in a vacuum oven to yield Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂. After the precursor was mixed with 5% excess LiOH·H₂O, the mixture was sintered at 750 °C for 12 h in flowing oxygen atmosphere to obtain NCA.

The structure and morphology of the sample were examined by X-ray diffraction (XRD, D/max-r A type Cu K_{α} , 40 kV, 300 mA), scanning electron microscopy (SEM, SU 3500) and transmission electron microscope (TEM, Tecnai G12), respectively. The contents of lithium, nickel, cobalt and aluminium of the sample were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300DV).

Coin-type CR2025 cells assembled in an argon filled glove box were used for the electrochemical testing of samples. The cell consisted of a lithium anode, a NCA cathode, a Celgard 2400 separator and an electrolyte of 1 mol L⁻¹ LiPF₆ in EC-DMC-EMC (1:1:1, volume ratio) solution. The cathode was composed of NCA, acetylene black and PVDF binder (8:1:1, weight ratio) on an aluminum foil. The charge-discharge tests were performed at a desired *C* rate in the range of 2.8-4.3 V (vs. Li/Li⁺) at 25 °C on a LAND CT2001A battery testing system (China). The thermal stability of NCA was investigated using differential scanning calorimetry (DSC) on TA Q600

from 100 to 350 °C at a rate of 5 °C ·min⁻¹ in a nitrogen environment. The DSC samples were prepared in the glove box from the disassembled cells which were charged at different states of charge (SOC) after cycling five times at 0.1 C.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the precursor Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ prepared by the co-precipitation method using C₄H₄O₆KNa·4H₂O as the chelating agent. It is seen that the diffraction peak positions of the precursor match well with the standard spectrum of JCPDS #01-1047. The XRD pattern of NCA synthesized from the precursor is presented in Fig. 1(b). Obviously, all the diffraction peaks of the asprepared NCA can be indexed to the pure α -NaFeO₂ hexagonal phase without any impurity. Furthermore, the perfectly ordered layered structure of the product is corroborated by the strong peak splitting of (006)/(012) and (018)/(110), high values of the c/a (~4.95) and $I_{(003)}/I_{(104)}$ (~1.33) ratios, and the low *R*-factor (*R*-factor = $(I_{(006)}+I_{(012)})/I_{(101)}$) of 0.39 [14].

The SEM images of the precursor and NCA are displayed in Fig. 2. As shown in Fig. 2(a), the spherical precursor powders with the size of 5-8 μm in diameter are comprised of primary needle-like particles. The morphology and size of NCA remain nearly the same as those of the precursor, except for the change of primary particles appearance into cylindrical form (Fig. 2(b)). This indicates that Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ and NCA prepared using C₄H₄O₆KNa·4H₂O as the chelating agent maintain the morphology of the corresponding products obtained with NH₃·H₂O [14]. Additionally, the composition analysis of NCA measured by ICP-AES shows that the molar ratio for Ni:Co:Al is 0.801:0.149:0.051, which is close to the targeted stoichiometry.

Fig. 3 exhibits the TEM images of NCA, where clear lattice fringes with the interplanar distance of 0.47 nm can be observed. The value corresponds to the d-

spacing of the (003) plane derived from Bragg equation (XRD pattern found in Fig. 1b). This suggests again that NCA can be prepared using C₄H₄O₆KNa·4H₂O as the chelating agent.

Both the initial charge/discharge curves at various C-rates and the cycle-life curve at 0.5 C of the sample are demonstrated in Fig. 4. Although the electrochemical polarization becomes severer with the increase of the C-rate, the sample exhibits good rate performance (Fig. 4(a)). The charge/discharge capacities at 0.1, 0.2, 0.5 and 1.0 C are found to be 245.6/204.4, 201.2/196.3, 189.0/182.2 and 177.3/171.4 mAh·g⁻¹, with the corresponding efficiencies of 83.2%, 97.6%, 96.4% and 96.7%, respectively. The cycle-life test at 0.5 C in Fig. 4(b) indicates that the charge/discharge capacities decreases from 189.0/182.2 to 173.7/166.8 mAh·g-1 after 100 cycles with the corresponding capacity retentions of 91.9%/91.5%, and the charge-discharge efficiency of each cycle maintains about 96%. Fig. 4(c) illustrates the DSC curves of charged $\text{Li}_x \text{Ni}_{0.8} \text{Co}_{0.15} \text{Al}_{0.05} \text{O}_2$ as a function of x (0 < x < 0.64) in the presence of the (The composition of fully delithiated the Li_{0.36}Ni_{0.8}Co_{0.15}Al_{0.05}O₂ (100% SOC), based on the discharge capacity.). At 0% SOC, no obvious exothermic peak can be observed. As the SOC increases, the exothermic peak shifts to lower temperature with increasing heat generation. At 100% SOC, the sample exhibits an exothermic peak at 231.8 °C with heat generation of 550.6 J·g⁻¹ which is related to oxygen generation from the decomposition of the cathode by reaction with the electrolyte [15]. These data are comparable to those of the reported NCA synthesized using other chelating agents [11-15]. However, this synthetic approach is more cost-effective and environment-friendly in the preparation of NCA compared to other co-precipitation methods, since the use of the 5-sulfosalicylic acid, EDTA and ammonia can be avoided.

4. Conclusions

C₄H₄O₆KNa·4H₂O is successfully used for the first time as the chelating agent in the co-precipitation method to prepare the precursor Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂. The NCA material synthesized from the precursor possesses spherical morphology and perfectly ordered layered structure. This is beneficial to its electrochemical properties with initial charge/discharge capacities of 245.6/204.4, 201.2/196.3, 189.0/182.2 and 177.3/171.4 mAh·g⁻¹ at 0.1, 0.2, 0.5 and 1.0 *C*, respectively, and charge/discharge capacity retentions of 91.9%/91.5% after 100 cycles at 0.5 *C*.

Acknowledgments

This project was supported by the Provincial Natural Science Foundation of Hunan, China (2017JJ2060) and China Scholarship Council (CSC201708430266).

References

- [1] J. Kim, H. Lee, H. Cha, M. Yoon, M. Park, J. Cho, Adv. Energy Mater. 8 (2018) 1702028.
- [2] W. Liu, H. Guo, M. Qin, J. Deng, L. Xu, S. Yi, T. Hong, ChemistrySelect 3 (2018) 7660-7666.
 - [3] N. Nitta, F. Wu, J. T. Lee, G. Yushin, Mater. Today 18 (2015) 252-264.
- [4] Y. Chen, P. Li, S. Zhao, Y. Zhuang, S. Zhao, Q. Zhou, RSC Adv. 7 (2017) 29233-29239.
- [5] W. Chen, Y. Li, D. Yang, X. Feng, X. Guan, L. Mi, Electrochim. Acta 190 (2016) 932-938.
 - [6] S. H. Ju, H. C. Jang, Y. C. Kang, Electrochim. Acta 52 (2007) 7286-7292.
 - [7] C. J. Han, J. H. Yoon, W. I. Cho, H. Jang, J. Power Sources 136 (2004) 132-138.
 - [8] S.B. Majumder, S. Nieto, R. S. Katiyar, J. Power Sources 154 (2006) 262-267.
 - [9] H. Ouyang, X. Li, Z. Wang, H. Guo, W. Peng, Z. He, Funct. Mater. Lett. 11

(2018) 1850083.

[10] M. Liang, D. Song, H. Zhang, X. Shi, Q. Wang, L. Zhang, ACS Appl. Mater. Interface 9 (2017) 38567-38574.

[11] H. Xie, K. Du, G. Hu, J. Duan, Z. Peng, Z. Zhang, J. Mater. Chem. A 3 (2015) 20236-20243.

[12] H. Xie, G. Hu, K. Du, Z. Peng, Y. Cao, J. Alloys Compd. 666 (2016) 84-87.

[13] M. Jo, M. Noh, P. Oh, Y. Kim, J. Cho, Adv. Energy Mater. 4 (2014) 1301583.

[14] G. Hu, W. Liu, Z. Peng, K. Du, Y. Cao, J. Power Sources 198 (2012) 258-263.

[15] W. Liu, X. Tang, M. Qin, G. Li, J. Deng, Mater. Lett. 185 (2016) 96-99.

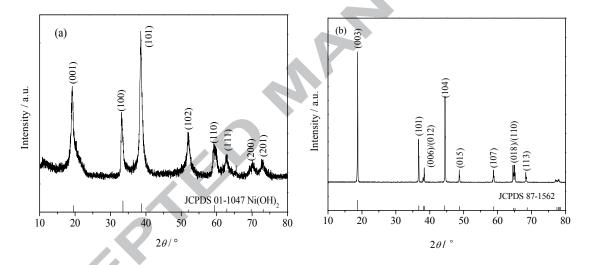


Fig. 1 XRD patterns of (a) Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ and (b) NCA.

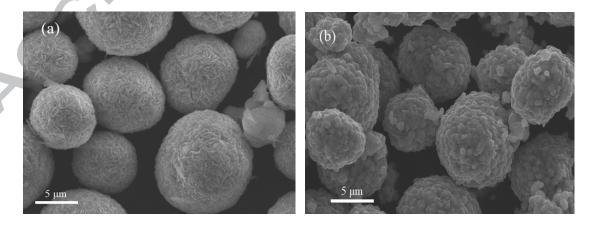


Fig. 2 SEM images of (a) Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ and (b) NCA.

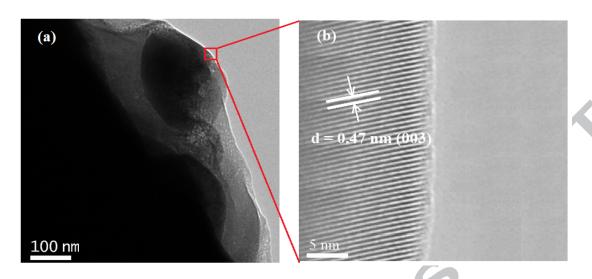


Fig.3 TEM images of NCA, (b) is the magnified image of the red frame region of (a).

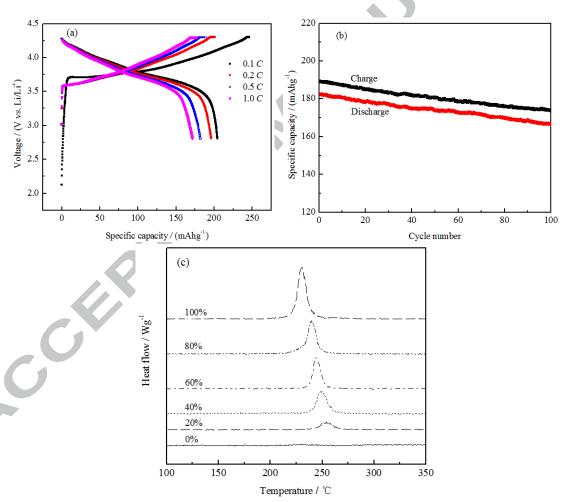


Fig. 4 (a) Initial charge/discharge curves at various *C*-rates, (b) cycle-life curves at 0.5

C and (c) DSC curves of NCA at different states of charge.

Highlights

> C₄H₄O₆KNa·4H₂O is used as a chelating agent to prepare Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂.

- > NCA prepared from this precursor shows excellent electrochemical properties.
- > This synthetic approach is more cost-effective and environment-friendly.

