Hydrothermal Synthesis and Electrochemical Performance of Micro-spherical LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Cathode Material

Chao Ma^{1,*}, Shuang-Yuan Tan^{2,*}

 ¹ School of Electronic Engineering, School of Microelectronics, Chengdu Technological University, Chengdu 611730, China
 ² Dongfeng Motor Co., Ltd, Dongfeng Nissan Passenger Vehicle Company, Guangzhou, 510800, China
 *E-mail: <u>chaoma@yahoo.com</u>, <u>tanshuangyuan@dfl.com.cn</u>

Received: 9 April 2020 / Accepted: 30 June 2020 / Published: 10 August 2020

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) as a cathode material for lithium-ion batteries was synthesized using a modified hydrothermal method. The NCM electrode exhibited a porous spherical microstructure and improved electrochemical performances compared to the sample prepared by the co-precipitation method. Further, it delivered a high initial discharge capacity of 174.4 mAh g⁻¹ at 0.2 C rate between 2.5 and 4.5 V, and a capacity of 123.8 mAh g⁻¹ was reached at 10 C after cycling at various rates. At the high rate of 10 C, the NCM showed an initial discharge capacity of 132.7 mAh g⁻¹ and with the capacity retention of 62.3 % after operating for 50 charge–discharge cycles. The excellent rate performance and cyclic stability can be ascribed to the porous structure with a large surface area that enhanced the chemical active nature of the cathode material, while providing more transport channels for the Li⁺ ions. These results indicate that the potential of the suggested method in tuning the morphology of the NCM cathode material to improve its electrochemical performance.

Keywords: Lithium-ion battery, cathode material, hydrothermal method, microsphere

1. INTRODUCTION

As a clean and reliable energy storage device, Lithium-ion batteries (LIBs) have been widely used in many fields, such as in portable electronic devices, hybrid, and full electric vehicles (EVs), utility power grids and so on. These applications greatly stimulate the development of LIBs, especially active materials, to meet the requirements of energy/power density, longevity and safety [1]. Due to the long cycle life and simple production process, LiCoO₂ has been the most widely used cathode material since the 1980s [2]. However, with the advent of EVs, LiCoO₂-based battery can no longer meet the requirement of high-energy applications. In addition, the disadvantages such as relatively high cost and

toxicity hinder the widespread use of LiCoO₂ material, thus encouraging the search for alternative materials [3]. The layered LiNi_{1-x-y}Co_xMn_yO₂ cathode materials have attracted significant attention owing to their low cost, low toxicity, and high energy density. Among these, the composition of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) is one of the most extensively studied and used to partially replace LiCoO₂ in many commercial batteries [4, 5].

It is well known that the physical properties of cathode materials such as morphology, particle size distribution, density, specific surface area, etc., synthesized by different methods, have a significant influence on the electrochemical properties of the LIBs [6]. Therefore, many efforts have been directed towards these aspects. Li et al. synthesized the cubic-shaped NCM powder by using a one-step hydrothermal method [6]. The enhanced surface area can be obtained due to the several small particles adhering to the surfaces of Al₂O₃-coated NCM particles, which can improve the rate performance of the NCM. Pi et al. prepared the disk-like NCM nanoplates with exposed (001) planes by following the Pechini method [7]. These cathode materials having a special microstructure and morphology achieved high capacity, enhanced rate performance and excellent cycling stability. Wang et al. indicated that the spherical morphology of the particles obtained in the synthesis of battery materials can lead to a high tap density and thereby impact the energy density of the LIBs, and facilitate the preparation of electrodes due to its excellent fluidity and dispersibility [8]. In addition, the spherical structure can provide a large amount of pore space for Li⁺ storage thereby increasing the specific capacity, and adapting to a volume change during the cycling [4]. Therefore, a convenient and economical method for synthesis of microspherical NCM cathode materials can not only improve the performance of LIBs but also promote the development of NCM cathode materials. In this work, a modified hydrothermal method for the preparation of micro-spherical NCM cathode materials has been proposed. The structure, morphology and electrochemical properties have been compared with those of the NCM cathode materials synthesized by conventional co-precipitation method.

2. EXPERIMENTAL

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders were synthesized by using Li₂CO₃ (AR, 99 %), NiSO₄·6H₂O (AR, 99 %), CoSO₄·7H₂O (AR, 99 %) and MnSO₄·H₂O (AR, 99 %) with the molar ratio of Li : Ni : Co : Mn maintained at 3.15 : 1 : 1 : 1 (5 % excess in molar ratio was kept to compensate for the volatilization of Li during the process of calcination). For the hydrothermal method, all metal sulfates were dissolved into deionized water and the total concentration of the solution was adjusted to 2 mol L⁻¹. After that, 0.2 mol L⁻¹ of Na₂CO₃ aqueous solution was added dropwise in the above metal sulfate solution until no more precipitate was formed. The mixture was then stirred at room temperature for 1 h. Afterwards, the as-prepared starting suspension was poured into a 100 ml Teflon-lined autoclave and sealed. The mixture was hydrothermally treated at 150 °C for 10 h followed by thorough washing to obtain the pink precursor, which was subsequently mixed with Li₂CO₃ and grinded. Next, the mixture was heated at 450 °C for 5 h in air. Finally, the as prepared powders were calcined at 850 °C in air for 10 h.

For the co-precipitation method, the first part of the synthesis was the same as that of the hydrothermal method. After the addition of Na₂CO₃ solution droplets to the metal sulfate solution, the

magnetic stirring was continued for 3 h. After the reaction was completed, the precipitate was allowed to stand for 5 h and subsequently washed and dried to obtain the precursor. After mixing with Li₂CO₃, the remaining steps were the same as that of the hydrothermal method. The products synthesized by the hydrothermal and co-precipitation methods were labeled as S1 and S2, respectively.

The crystal structure of the prepared cathode material was analyzed by X-ray diffraction (XRD, Bruker D8) and the particle morphology of the NCM powder was characterized by scanning electron microscopy (SEM, Supra55VP, Zeiss). The Brunauer–Emmett–Teller (BET) specific surface area of the sample was obtained by N₂ adsorption/desorption measurement (SA3100, Beckman Coulter).

Electrochemical characterizations were carried out using the CR2025 type coin cells. The cathode was fabricated by casting a slurry of 80 wt % prepared active material, 10 wt % acetylene black and 10 wt % polyvinylidene fluoride (PVDF) in 1-methy-1-pyrrolidinone solvent onto an aluminum foil. In the next step, the cathode foil was cut into circular discs of 1 cm diameter and dried at 100 °C for 12 h in vacuum. The cells were assembled in an Ar-filled glovebox using a lithium metal foil as the counter electrode. The electrolyte was 1 mol L⁻¹ LiPF₆ in a mixture of ethyl carbonate, propylene carbonate, ethyl methyl carbonate and butyl acetate. They were charged and discharged over a voltage range between 2.5 and 4.5 V with current densities ranging from 0.2 to 10 C rates (1 C = 200 mAh g⁻¹) on a multi-channel battery testing system (BTS-51, Neware, China). Electrochemical impedance spectroscopy (EIS) was measured on an electrochemical workstation (CHI650, Chenhua, China).



3. RESULTS AND DISCUSSION

Figure 1. XRD patterns of samples prepared by hydrothermal method (S1) and co-precipitation method (S2).

Fig.1 shows the XRD patterns of the two kinds of NCM powders prepared by the hydrothermal and co-precipitation methods, respectively. All the diffraction peaks in the two samples can be attributed to the hexagonal α -NaFeO₂ structure having a *R-3m* space group, and no additional diffraction peaks related to the secondary phases or impurities have been found. The strong and narrow diffraction peaks along with the obvious peak splits of (006)/(102) and (108)/(110) in the S2 sample reveal the presence of ordered layer-structure [9]. The intensity of the peak in the S1 sample is significantly weaker than that in the S2 sample. In addition, the peak width becomes broad and the peak position remains unchanged, indicating that the average grain size of the S1 sample is reduced [10].



Figure 2. SEM images of (a) S1, (b) S2 samples, and (c, d) precursor powders of the S2 sample after hydrothermal reaction.

To explore the influence of the synthesis methods on the surface morphology, SEM was used to analyze the morphologies and microstructures of the NCM samples. As evident from the SEM images depicted in Fig. 2, the samples synthesized by the two methods exhibit completely different morphologies. The S1 sample has a spherical structure in which the secondary particles consist of densely aggregated submicron-sized primary particles. The microspheres are distributed homogeneously with sizes of about 2 μ m in diameter. In addition, more active sites and three-dimensional channels can be provided for Li⁺ ions diffusion as the primary particles attach to the surface to form a porous structure. The unique structure of the NCM synthesized by the hydrothermal method is mainly due to the template formed by the precursor. As shown in Fig. 2c, d, after the completion of the hydrothermal reaction, pollen-like precursor powders are obtained, with an average size of about 1.5–3.0 µm. It can be clearly

seen that the precursor powder has a very regular microsphere like shape, consisting of further assembly of fine particles. It is predicted that the NCM grains grow along the radial direction of the precursor microspheres and eventually form large agglomerated NCM particles on the surface. For the sample S2, the particles present irregular cubes with a diameter of about 1 μ m and a very smooth surface. The specific surface areas of S1 and S2 samples are measured to be 16.89 and 10.17 m² g⁻¹, respectively. It is believed that a higher specific surface area has a good influence on the electrochemical performance of the cathode material [11].



Figure 3. Rate performances of NCM cathode materials synthesized by hydrothermal (S1) and coprecipitation methods (S2) as rates from 0.2 to 10 C in the voltage range from 2.5 to 4.5 V.

Fig. 3 shows the discharge capacities of NCM cathode materials recorded at various rates, ranging from 0.2 to 10 C with five cycles of operation at each rate, and finally back to 0.2 C. It is seen that with the gradual increase in current density, the discharge capacities of the two samples are rapidly reduced. After subjecting the sample to long stress period and high rate cycles, the two samples recover their specific discharge capacities at the low rate of 0.2 C, indicating that the NCM samples synthesized by both hydrothermal and co-precipitation methods have good reversibility. It can also be seen that the two NCM cathode materials have similar discharge specific capacities at low rates of 0.2 and 0.5 C. Further, the sample prepared by co-precipitation method has a discharge capacity of 184.0 mAh g⁻¹ at the low-rate cycle, which is slightly higher than the value of 178.1 mAh g⁻¹ of the NCM prepared by the hydrothermal method. However, the performance of the S1 sample is significantly improved when the charge/discharge rate is greater than 1 C. The discharge capacity of the S1 sample at 10 C is 123.8 mAh g⁻¹, which is much higher than the value for S2 sample (93.5 mAh g⁻¹). The ratio of the discharge capacity

at 10 C and 0.2 C for S1 sample is 69.5 %, which is higher than that of S2 sample (50.8%), indicating that the NCM sample prepared by hydrothermal method possesses better reversibility at high rates. The slow solid state diffusion of Li⁺ ions was considered as a vital factor for the limitation in rate capability [12]. The porous spherical structure in the NCM leads to an effective increase in the specific surface area of the active material, and the porous structure on the surface forms a three-dimensional tunnel for the diffusion of Li⁺ ions, thereby effectively increasing the specific capacity at the high-rate charge/discharge processes.



Figure 4. The initial charge–discharge curves of NCM cathode materials at 0.2 C rate and the charge–discharge curves after various cycles at 10 C (dash curve).

The initial charge–discharge curves of the two samples recorded at 0.2 C rate and the charge– discharge curves after various cycles at 10 C are shown in Fig. 4. All the curves are obtained to be smooth and regular illustrating the structural stability of the NCM electrode in the test voltage range [7]. Both the samples show a gradual decrease in the discharge voltage from 4.5 to 2.5 V at 0.2 C rate, which is the main characteristic of the NCM cathode material [9]. The initial charge/discharge capacities for the S1 and S2 samples are 204.9/174.4 mAh g⁻¹ and 228.6/176.7 mAh g⁻¹ respectively, corresponding to coulombic efficiencies of 85.1 % and 77.3 %. The S1 sample has a lower initial discharge capacity, but the coulombic efficiency is much higher than that of the S2 sample. The charge voltage of the S1 sample is nearly same as that of the sample S2, while the discharge voltage is higher, indicating that the smaller electrode polarization exists in the S1 electrode [9]. While the discharge rate increases to 10 C, the discharge capacity of the S1 sample is higher than that of S2. In addition, the plateaus become shorter and the differences between the charge and discharge plateaus become larger at 10 C, which can be attributed to the electrode polarization at high rates [6]. The differences of the charge and discharge plateaus of the S1 sample at 10 C rate is much smaller compared to the S2 sample, suggesting an improved reversibility during the deintercalation/intercalation process of Li⁺ ions and a reduced capacity attenuation during battery cycling at high charge/discharge rate for MCN synthesized by hydrothermal method.



Figure 5. Cycling performances of NCM cathode materials synthesized by hydrothermal (S1) and coprecipitation methods (S2) at 10 C rate.

To further compare the cycling performances of the two samples at high rates, the cells are charged and discharged 50 cycles at a rate of 10 C in the voltage range from 2.5 to 4.5 V at room temperature. As shown in Fig. 5, the corresponding discharge capacities indicate a significant improvement in the cycling performance of the sample S1. The highest discharge capacity of the S1 electrode reaches 132.7 mAh g⁻¹ and its capacity retention over 50 cycles of operation is 62.3%. However, the sample S2 delivers lower discharge capacity of 123.9 mAh g⁻¹ and lower capacity retention of 46.2 %. The results demonstrate that the porous spherical NCM cathode material synthesized by hydrothermal method has better cyclability compared with the sample prepared by the usual coprecipitation method. It can be speculated that the improved capacity retention is mainly due to the large surface area of the active material placed in contact with the electrolyte and the short diffusion distance provided by the submicron primary particles, which both facilitate the insertion and extraction of Li⁺ ions [13, 14]. Furthermore, its excellent cycling performance can be attributed to the suppression of the increase in charge transfer resistance during the cycling process. Compared to the previously reported NCM cathode materials, the sample obtained by the modified hydrothermal method in the present study

offers a considerable potential for applications at high discharge rates. The comparative results of the different NCM cathode materials in terms of the synthesis method, structure and cycling performance are shown in Table 1.

Cathode material	Synthesis method	Structure	Cycling performance (rate, cycles, initial/final capacity)
NCM [15]	Template-sacrificial method	Hollow hemisphere	0.2 C, 50, 196/176 mAh g ⁻¹
NCM [16]	Ethylene glycol-assisted sol-gel method	Cubic with larger specific surface area	0.2 C, 50, 208/168 mAh g ⁻¹
NCM [17]	Thermal decomposition solid state reaction	Ultrafine particle	1 C, 200, 161/134 mAh g ⁻¹
NCM [18]	Electrospinning method	Nanofiber	5 C, 200, 100/71 mAh g ⁻¹
NCM in this work	Modified hydrothermal method	Microsphere structure	10 C, 50, 133/83 mAh g ⁻¹

Table 1. Comparison of different NCM cathode materials in terms of the synthesis method, structure and cycling performance.



Figure 6. Nyquist spectra of NCM cathode materials synthesized by hydrothermal (S1) and coprecipitation methods (S2).

To determine the underlying physical reason behind these results, the EIS is employed to analyze the impedance of the electrodes at room temperature. As shown in Fig. 6, the Nyquist plots of the two samples consist of a semicircle at the high-to-medium frequency range and an oblique line corresponding to the low frequency region. In general, the semicircle in high-to-medium frequency range is associated with the charge transfer resistance (R_{ct}), and the oblique line is attributed to the Warburg impedance associated with the Li⁺ diffusion in the electrodes [19]. The values of R_{ct} are related with the diameter of the semicircle at the interface of the crystalline particles and indicate the formation of an electrode/electrolyte interface layer on the surface of the cathode after the operation of the charge– discharge cycle [20]. As can be seen from Fig. 6, the R_{ct} of the S1 sample is significantly smaller than that of the S2 sample, which facilitates the transport of Li⁺ ions between the electrode and electrolyte, thereby reducing the reaction resistance [21]. This can also explain why the NCM cathode material synthesized by the hydrothermal method has better electrochemical performance. Further, it should be noted that the porous spherical structure, equipped with a large surface area, can effectively improve the surface chemical activity of the cathode material, and increase the electrode conductivity, thereby

4. CONCLUSIONS

In this paper, we report a modified hydrothermal method to synthesize the NCM cathode material having a porous spherical structure with large surface area, in which a large number of submicron primary particles adhere to the surface, which facilitate the Li⁺ transport during the battery operation. This NCM material not only exhibits a particular microstructure and morphology, but more importantly, it is endowed with enhanced rate performance and excellent cycling stability compared with the sample synthesized by the conventional co-precipitation method. The improved electrochemical properties can be attributed to the smaller electrode polarization and larger electrode conductivity.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 61904020).

References

1. J. B. Goodenough, K. S. Park, J. Am. Chem. Soc., 135 (2013) 1167.

improving the rate capability and cycle life of the battery.

- 2. K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, Solid State Ionics, 3-4 (1981) 171.
- 3. P. He, H. Wang, L. Qi, T. Osaka, J. Power Sources, 160 (2006) 627.
- 4. J. B. Zhang, Z. G. Wu, W. B. Hua, H. Liu, B. H. Zhong, *Ionics*, 21 (2015) 3151.
- G. H. Lee, J. Wu, D. Kim, K. Cho, M. Cho, W. Yang, Y. M. Kang, Angew. Chem. Int. Edit., 59 (2020) 8681.
- 6. X. Li, W. He, L. Chen, W. Guo, J. Chen, Z. Xiao, *Ionics*, 20 (2013) 833.
- 7. W. Pi, T. Mei, Z. Zhang, X. Li, J. Wang, J. Li, X. Wang, CrystEngComm, 19 (2017) 442.
- 8. Y. Wang, Y. Yang, Y. Yang, H. Shao, Mater. Res. Bull., 44 (2009) 2139.
- 9. S. Y. Tan, L. Wang, L. Bian, J. B. Xu, W. Ren, P. F. Hu, A. M. Chang, J. Power Sources, 277

(2015) 139.

- 10. C. Ma, W. Ren, L. Wang, J. B. Xu, A. M. Chang, L. Bian, J. Eur. Ceram. Soc., 36 (2016) 4059.
- 11. Y. Ding, P. Zhang, Z. Long, Y. Jiang, F. Xu, J. Alloy. Compd., 487 (2009) 507.
- 12. Y. Ding, P. Zhang, Z. Long, Y. Jiang, D. Gao, J. Alloy. Compd., 462 (2008) 340.
- J. Kasnatscheew, M. Evertz, B. Streipert, R. Wagner, R. Klöpsch, B. Vortmann, H. Hahn, S. Nowak, M. Amereller, A. C. Gentschev, P. Lamp, M. Winter, *Phys. Chem. Chem. Phys.*, 18 (2016) 3956.
- 14. M. Yuan, Y. Li, Q. Chen, C. Chen, X. Liu, W. Zeng, R. Wang, S. Xiao, *Electrochim. Acta*, 323 (2019) 134822.
- 15. Z. Y. Li, H. L. Zhang, Int. J. Electrochem. Sci., 14 (2019) 3524.
- 16. L. Zhu, G. Yang, J. Liu, C. Bao, L. Xie, X. Cao, ChemistrySelect, 4 (2019) 11475.
- 17. F. Xu, H. Yan, J. Chen, Z. Zhang, C. Fan, J. Appl. Electrochem., 49 (2019) 647.
- 18. C. Lv, J. Yang, Y. Peng, X. Duan, J. Ma, Q. Li, T. Wang, *Electrochim. Acta*, 297 (2019) 258.
- 19. J. Dou, X. Kang, T. Wumaier, H. Yu, N. Hua, Y. Han, G. Xu, J. Solid. State. Electr., 16 (2011) 1481.
- 20. C. Ma, L. Luo, K. W. Li, B, Zhou, Q. Shi, Int. J. Electrochem. Sci., 14 (2019) 7643.
- 21. P. Shi, G. Qu, S. Cai, Y. Kang, T. Fa, X. Chen, J. Am. Ceram. Soc., 101 (2018) 4076.

© 2020 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).