Dear Ming Wang, Hongling Bao, Liang Du, Pengtao Qi, Xueming Zhang **Paper ID:** MT909

Paper Title: Preparation and electrochemical performance of Li4Ti5O12/Co3O4 composite as an anode of Lithium-ion battery

We are pleased to inform you that your paper has been accepted. This notification serves as our formal acceptance of your paper. Please note that this NOTIFICATION will be sent to your co-author(s) (if any), as well.

You must finish the following FOUR processes and register by Email. Authors must strictly follow the manuscript preparation instructions and reference style. Please take the following instructions to prepare the final manuscript:

1. Finish the payment of Registration fee according to the Registration Form.

2. Format your paper or abstract according to the Template

3. Fill and Submit the Copyright Transfer Agreement (fill in the blank and sign your name by hand, finally scan your Copyright Transfer Agreement as PDF file);

4. Send your Filled Registration Form (English/Chinese); Final Paper (both .doc and .pdf format);

The Scanned Payment Proof (in jpg format) and Scanned Copyright Agreement (in pdf format).

If the above requirements are met by the set deadlines, the papers will be published by TTP in "Solid State Phenomena" proceedings which should be submitted to EI Compendex. Please strictly adhere to the format specified in the conference template while preparing your final paper, and submit all the files to the email: cfp@icmtm.org (Before 18:00, September 30, 2021)

If you have any problem when preparing the final paper, please feel free to contact us via <u>cfp@icmtm.org</u> by quoting your Paper ID in all the following procedures and any future inquiries.

Thank you for your contribution to the conference and we are looking forward to your future participation!

Preparation and electrochemical performance of Li₄Ti₅O₁₂/Co₃O₄

composite as an anode of Lithium-ion battery

Ming Wang*, Hongling Bao, Liang Du, Pengtao Qi, Xueming Zhang

School of Materials Science and Engineering, Liaoning Technical University, 47 Zhonghua Road, 123000 Fuxin, China

Email: wangming@Intu.edu.cn

Key words: Lithium-ion battery; Li₄Ti₅O₁₂; Composite; Electrochemical performance

Abstract: The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Co}_3\text{O}_4$ composites were prepared by hydrothermal reaction method with different Co_3O_4 mass content (3%, 7%, 11%, and 15%). The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nano particles were set in-situ on the Co_3O_4 sheet. Co ion was doped into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice. The first cycle specific capacity firstly increased and then decreased with Co_3O_4 content increasing, which the discharge capacity reached the peaking value that the first capacity was 1111 mAh/g and the specific discharge capacity retained 240 mAh/g after 200 cycles. After 200 cycles of charge and discharge, the retention of the capacity was 96.4% at 0.1 A/g, and the retention of the capacity was 98.4% at 0.5 A/g.

0 Introduction

With the development and progress of human society, building a low-carbon society supported by sustainable energy is a topic of worldwide concern ^[1~3]. Lithium-ion batteries have been widely used in electric vehicles and mobile devices because of their advantages such as high energy density, long service life and small environmental pollution ^[4–9]. However, the fire and explosion accidents of electric vehicle batteries in recent years show that lithium-ion batteries still have some potential safety risks, which hinder the rapid development and wide application of lithium-ion batteries ^[10-14]. Developing new electrode materials or modifying and improving existing electrode materials is one of the methods to solve the above problems ^[15,16]. In the process of cycling, graphite anode batteries will suffer structural damage and irreversible capacity loss due to lithium precipitation, which is difficult to meet the requirements of high ratio and long life. In order to overcome these shortcomings, research on lithium titanate (Li₄Ti₅O₁₂, LTO) anode materials has gradually become a hot spot ^[17~19]. With advantages such as long cycle life, fast charge-discharge rate and stable structure during charge-discharge, it is used as a high-power lithium battery with long cycle life ^[20~22]. However, the low conductivity, poor lithium diffusion performance and low power density limit the practical application of LTO ^[23~27].

So far, metallic ion modification of lithium titanate is an effective method to improve the conductivity of the material. In this paper, the modification of LTO/Co_3O_4 composite was studied by the hydrothermal reaction of LTO particles in situ on the Co_3O_4 sheet. The research results can not only improve the high specific capacity and the ratio, but also the simple process, low production cost, suitable for industrial production. It provides theoretical reference for promoting and promoting the progress of LTO technology, realizing industrial production, and provides theoretical basis and ideas for the commercial application of LTO composite materials.

1 Experimental

 α -Co(OH)₂ was used as cobalt source, LiOH was lithium source and TiO₂ was titanium source. Firstly, α -Co(OH)₂ was prepared by the reaction of CoCl₂ and ammonia water, and then LiOH and TiO₂ were weighed according to the molar ratio of 4:5. Co_3O_4 with different contents (3%, 7%, 11% and 15%) could be calculated by α -Co(OH)₂. Finally, different proportions of α -Co(OH)₂ were reduced with LiOH and TiO₂ by hydrothermal reaction. After natural cooling, the solution was taken out, put into the electric blast drying oven to dry, and then calcined at 800 °C for 4 h in the tubular furnace to obtain the product, and assembled with the button battery of 2025 model.

2 Results and discussion

2.1 Microstructure characterization of LTO and LTO/Co₃O₄ Composites

Figure 1 shows the XRD patterns of LTO/Co₃O₄ at different proportions. As can be seen from Figure 1, the diffraction peak of activated LTO/Co₃O₄ composite conforms to [JCPDS 49-0207], and the characteristic diffraction peaks of LTO appear at 18.3 $^{\circ}$, 35.6 $^{\circ}$, 47.2 $^{\circ}$, 62.8 $^{\circ}$ and 66.1 $^{\circ}$, which the corresponding crystal plane is (111), (311), (331), (440) and (531), respectively. With the increasing content of Co₃O₄, the diffraction peak of (111) plane gradually shifts to the right, because the radius of Co ion (1.26 Å) was smaller than that of Ti ion (1.45 Å), and the doping enters into the LTO lattice, causing the diffraction peak shifts to the higher diffraction angle.



Fig.1 XRD patterns of LTO/Co₃O₄ with different Co₃O₄ contents.

Figure 2 is the SEM images of LTO particles and LTO/Co₃O₄ composite with different Co₃O₄ contents, which Co₃O₄ content was corresponding to 7%, 11% and 15%, respectively. It can be seen from Figure 2(a) that the LTO particles with the size of approximately 200 nm were clean and angular, and the distribution was relatively uniform. The lamellar Co₃O₄ and LTO spherical particles distributed uniformly around Co₃O₄ or attached to the surface of Co₃O₄ in the different proportional composites. From Figure 2(b), when Co₃O₄ content was 7%, Li₄Ti₅O₁₂ particles appear slight agglomeration phenomenon. In Figure 2(c), when Co₃O₄ content reaches 11%, Li₄Ti₅O₁₂ and Co₃O₄ particles ware evenly dispersed and have the smallest particle size. This grain refinement also increases the specific surface area of the material to a certain extent. In Figure 2(d), agglomeration of Li₄Ti₅O₁₂ particles centered on Co₃O₄ occurs when the Co₃O₄ content reaches 15%. In Figure 2(d), the contact between Co₃O₄ sheets was relatively close. Such agglomerations of Li₄Ti₅O₁₂ and Co₃O₄ may affect the specific capacity of composites.



Fig. 2 SEM images of LTO and LTO/Co₃O₄ composites with different Co₃O₄ contents. (a) LTO; (b)

2.2 Electrochemical properties of LTO and LTO/Co₃O₄ Composites

Figure 3 shows the EIS (AC impedance) test results of LTO/Co₃O₄ composites with different ratios. It can be seen from the figure that the internal resistance of LTO/Co₃O₄ composites was 2.5 Ω . The charge transfer impedances are 29.5 Ω , 27.5 Ω , 24 Ω and 27.8 Ω , respectively, corresponding to Co₃O₄ content~3%, 7%, 11%, 15%. It can be found that with the increase of Co₃O₄ addition amount, the charge transfer impedance of the composite decreases first and then increases. With the increase to 10.5%, the charge transfer impedance first decreases because Co₃O₄ doping increases the conductivity of the material, while the charge transfer impedance of 11%-15% increases because excessive Co₃O₄ agglomeration occurs with the increase of Co₃O₄ content, resulting in the reduction of the specific surface area of the composite. In the built-in diagram, Rs is ohmic resistance, CDI (capacitive effect between positive and negative electrodes) is the double capacitance between electrode and electrolyte, and ZF is the series connection between RCT (charge transfer resistance) and ZW (Warburg impedance).



Fig.3 EIS (AC impedance) test of LTO/Co₃O₄ (Built-in diagram is equivalent circuit diagram)

Figure 4 shows the charge-discharge curves of LTO/Co₃O₄ composite materials with different mass fractions of Co_3O_4 in the first two weeks at 0.1A/g. In figure 4(a), (b), (c) and (d), the specific discharge capacities of the first cycle are 598, 756, 1111and 1023mAh/g, respectively; The coulombic efficiency of the first charge and discharge is 36.95%, 66.14%, 83.16% and 68.23%, respectively. Among these ratios, the charge-discharge ratio of the first cycle increased first and then decreased (gradually increased from 3% to 11%, and gradually decreased from 11% to 15%), and the highest ratio was 10.5%. The lowest charge-discharge capacity of the first cycle is corresponding to the ratio~3%. The initial charge-discharge specific capacity of the four groups is much higher than the theoretical specific capacity of LTO (175 mAh/g), which indicates that LTO/Co₃O₄ composite material has a very obvious effect on the improvement of the initial charge-discharge specific capacity of LTO. As the proportion increases, the specific surface area in the composite decreases gradually, so the specific capacity increases first and then decreases with the increase of Co_3O_4 doping amount. The discharge specific capacities of (a), (b), (c) and (d) in the second cycle are 181, 317, 518 and 450 mAh/g, respectively. The coulomb efficiencies in the second week were 88.95%, 53.94%, 76.83% and 71.33%, respectively. As can be seen from Fig. 4, the discharge specific capacity of the composite material in the first week and the second week has a large difference, but the charging specific capacity does not. This is because the SEI film is formed in the first cycle, which consumes part of lithium and leads to irreversible capacity loss. As a result, Co_3O_4 is slightly higher than the theoretical specific capacity of Co_3O_4 (900 mAh/g).



Fig. 4 Charge-discharge curves of LTO/ Co_3O_4 composites with different Co_3O_4 contents. (a)3%; (b)7%; (c)11%; (d)15%

Figure 5 (a) shows the rate performance of four LTO/Co_3O_4 composites with different proportions at the same current density for 200 cycles. The composites were cycled for 40 cycles at 0.1, 0.5, 1.0, 0.5 and 0.1 A/g, respectively.

As can be seen from the figure, the multiplier performance of the four groups firstly increased and then decreased with the increase of proportion $(3\% \sim 11\%$ gradually increased, $11\% \sim 15\%$ gradually decreased). The ratio with the best ratio was 11%. the retention rate of 0.1A/g capacity is 96.4%, and that of 0.5A/g capacity is 98.4%.

Figure 5 (b) shows the cycle performance of the composite material with $Co_3O_4 = 11\%$, and the current density is 0.1 A/g. It can be seen from the figure that the specific capacity of the composite material attenuates to A great extent in the first few weeks, and then becomes stable gradually. This is because the first specific capacity of Co_3O_4 is high in the process of charging and discharging, and SEI film is easily generated. With the increase of cyclic process, the cyclic characteristics of composites gradually show the high cyclic stability of lithium titanate. The specific capacity of the material is maintained to 240 mAh/g.



Fig.5 (a) Charge-discharge curves of LTO/Co₃O₄ composites with different proportions 3%; 7%; 11%; 15%. (b) Cycle performance of the composite material with LTO and LTO/Co₃O₄ (11%)

3 Conclusions

(1)LTO particle distribution is uniform, LTO/Co₃O₄ composite particle size is small, Co_3O_4 lamellar carrier effect is more ideal. The properties of LTO/Co₃O₄ composites synthesized by hydrothermal method are better.

(2)The discharge capacity of LTO/Co₃O₄ composite increases first and then decreases. The performance of LTO/Co₃O₄ composite with 11% mass ratio is better. The discharge capacity of LTO/Co₃O₄ composite is 1111 mAh/g for the first discharge and 240 mAh/g after 200 cycles. After 200 cycles of charge-discharge cycle, the retention rate of 0.1 A/g capacity was 96.4% compared with that at the 40th cycle. Compared with the capacity at 80 cycles, the capacity retention rate of 0.5 A/g reached 98.4%.

Acknowledgement

This work was supported by General Project of Science Research Foundation of Liaoning Province (LJKZ0363) and Discipline Innovation Team Project of Liaoning Technical University (LNTU20TD-09 and LNTU20TD-16).

Reference

[1] Li L, Xu Y. Development status and trend analysis of lithium ion power battery[J]. China Manganese Industry, 2020, 38(05): 9-13+21.

[2] Liu Y, Zhang R, Wang J, et al. Current and future lithium-ion battery manufacturing[J]. Science, 2021, 24(4): 1023-1030.

[3] Tian H X, Qin P, et al. A review of the state of health for lithium-ion batteries: Research status and suggestions[J]. Journal of Cleaner Production, 2020, 261(8):120813.1-120813.30.

[4] Yan H, Zhang D, Qi, et al. A review of spinel lithium titanate ($Li_4Ti_5O_{12}$) as electrode material for advanced energy storage devices[J]. Ceramics International, 2021, 47(5): 5870-5895.

[5] Yang Y, Okonkwo E G, Huang G, et al. On the sustainability of lithium on battery industry–A review and perspective[J]. Energy Storage Materials, 2021, 36(5): 186-212.

[6] Yi T F, Wei T T, Li Y, et al. Efforts on enhancing the li-ion diffusion coefficient and electronic conductivity of titanate-based anode materials for advanced Li-ion batteries[J]. Energy Storage Materials, 2020, 26: 165-197.

[7] Tang Y, Yue F, Guo X Y, et al. The next generation of electrochemical energy storage technology of the international development trend analysis[J]. Energy Storage Science and Technology, 2021, 49(8):1-9.

[8] Vikram Babu B, Redd M S, Chandana G, et al. Microstructural, impedance and conductivity studies of magnesium doped lithium titanate materials for li-ion batteries[J]. Materials Today: Proceedings, 2021, 43(47): 1539-1544.

[9] Ji G, Ma Y, Ding B, et al. Improving the performance of high capacity li-ion anode materials by lithium titanate surface coating[J]. Chemistry of Materials, 2012, 24(17): 3329-3334.

[10] Hu Y X, Zhao G J. Application and safety analysis of lithium ion battery in energy storage[J]. Power Supply Technology, 2021, 45(01): 119-122.

[11] Li J, Zhu Y, Wang L, et al. Lithium titanate epitaxial coating on spinel lithium manganese oxide surface for improving the performance of lithium storage capability[J]. ACS Applied Materials Interfaces, 2014, 6(21): 18742-18750.

[12] Lai Y L, Yang K, Liu H, et al. Review of safety warning methods for lithium ion batteries [J]. Energy Storage Science and Technology, 2020, 9(06): 1926-1932.

[13] Yang B, Cui N X, Wang M C. Internal short circuit fault diagnosis for lithium-ion battery based on voltage and temperature[C]. Proceedings of the third Annual Conference of Vehicle Control and Intelligence Committee of Chinese Association of Automation. 2019,28(09): 1-6.

[14] Muhammad R, Muhammad A. Understanding the low temperature electrochemistry of magnesium-lithium hybrid ion battery in all--phenyl--complex solutions[J]. Journal of Energy Chemistry, 2021, 56(38): 383-390.

[15] Yang X, Zhan C, Ren X, et al. Nitrogen-doped hollow graphite granule as anode materials for high-performance lithium-ion batteries[J]. Journal of Solid State Chemistry, 2021, 303(09):453-460.

[16] Zhou Z R, Zhang Y J, Dong P, et al. Research overview of lithium ion battery cathode material[J]. Nonferrous Equipment, 2020(02): 7-11.

[17] Luo J, Tian G L, Zhang L L, et al. Review on lithium ion battery system of lithium titanate[J]. Power Supply Technology, 2019, 43(04): 693-695.

[18] Zhang Q, Liu Y, Lu H, et al. Ce³⁺ -doped Li₄Ti₅O₁₂ with CeO₂ surface modification by a sol-gel method for high-performance lithium-ion batteries[J]. 2016, 189(05): 147-157.

[19] Feng Y, Wu K, Deng X, et al. Exfoliated graphite nanosheets coating on nano-grained $SnO_2/Li_4Ti_5O_{12}$ as a high-performance anode material for lithium-ion batteries[J]. Langmuir, 2020, 36(48): 14666-14675.

[20] Li S, Mao J. The influence of different types of graphene on the lithium titanate anode materials of a lithium ion battery[J]. Journal of Electronic Materials, 2018, 47(9): 5410-5416.

[21] Maloney R P, Kim H J, Sakamoto J S. Lithium titanate aerogel for advanced lithium-ion batteries[J]. ACS Appl Mater Interfaces, 2012, 4(5): 2318-2321.

[22] Wang J, Ge B, Li H, et al. Challenges and progresses of lithium-metal batteries[J]. Chemical Engineering Journal, 2021, 420(02):746-755.

[23] Tan Y, Xue B.Research progress of lithium titanate as anode material for lithium ion battery[J]. Journal of Inorganic Materials. 2018, 33(05): 475-482.

[24] Zhang F, Yi F, Meng T, et al. In situ supramolecular self-assembly assisted synthesis of LTO– carbon-reduced graphene oxide microspheres for lithium-ion batteries[J]. ACS Sustainable Chemistry & Engineering, 2018, 7(1): 916-924.

[25] Stenina I A, Shaydullin R R, Desyatov A V, et al. Effect of carbon and n-doped carbon nanomaterials on the electrochemical performance of lithium titanate-based composites[J]. Electrochimica Acta, 2020, 364(13):892-899.

[26] Huang F, Ma J, Xia H, et al. Capacity loss mechanism of the LTO microsphere anode of lithium-ion batteries at high temperature and rate cycling conditions[J]. ACS Applied Materials Interfaces, 2019, 11(40): 37357-37364.
[27] Wang Q, Wang H, Wu J, et al. Advanced electrolyte design for stable lithium metal anode: from liquid to solid[J]. Nano Energy, 2021, 80(54):945-954.