Fabrication of Li$_4$Ti$_5$O$_{12}$@CN Composite With Enhanced Rate Properties

Hui Xiao$^1$, Xiaobing Huang$^{2*}$, Yurong Ren$^1*$, Xiang Ding$^2$ and Shibiao Zhou$^2$

$^1$ School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Changzhou University, Changzhou, China, $^2$ Hunan Province Cooperative Innovation Center for The Construction and Development of Dongting Lake Ecological Economic Zone, College of Chemistry and Materials Engineering, Hunan University of Arts and Sciences, Changde, China

Folic acid is first time applied as a carbon-nitrogen precursor to fabricate Li$_4$Ti$_5$O$_{12}$@CN composites via ball milling Nano-TiO$_2$, Li$_2$CO$_3$ and folic acid with ethanol as solvent, and then followed by heating treatment in argon. XRD, SEM, TEM, XPS, charge-discharge test and EIS are used to evaluate the influence of N-doped carbon coating on its structure, morphologies and electrochemical property. It is demonstrated that the N-doped carbon coated Li$_4$Ti$_5$O$_{12}$ composite exhibits superior high-rate performance compared with pure Li$_4$Ti$_5$O$_{12}$. It possesses a high discharge capacity of 174, 165 mAh g$^{-1}$ at 0.5 and 10 C, respectively. Additionally, an initial specific capacity of 96.2% is obtained after 200 cycles at 10 C. The remarkable performance might be put down to the N-doped carbon layer providing efficiently electron conductive network and nanosized decreasing lithium ion diffusion path.

Keywords: Li-ion batteries, anode material, folic acid, Li$_4$Ti$_5$O$_{12}$, N-doped carbon coating

INTRODUCTION

In the past few years, carbon materials have been regarded as the most commercially valued lithium battery anode material (Ma et al., 2016; Long et al., 2017; Li et al., 2019; Wu et al., 2019). Unfortunately, its low lithiation potential ($\sim$0.2 V vs. Li$^+/Li$) will result in the activation of dendritic lithium, thus further creating safety problems. Moreover, insufficient diffusion coefficient of lithium ion and large volume change will result in poor rate performance and cycle stability (Han et al., 2018; Yi et al., 2018). Nevertheless, its small diffusion coefficients (10$^{-9}$ ∼10$^{-13}$ cm$^2$ S$^{-1}$) and weak electrical conductivity ($\sim$10$^{-13}$ S cm$^{-1}$) (Jiang et al., 2017), resulting in serious electrode polarization and poor capability at high current density, has been considered as the main bottleneck of its commercial application for high-power LIBs. In order to overcome this problem, several strategies have been suggested by researchers, including synthesis of Li$_4$Ti$_5$O$_{12}$ with porous structure (Lu et al., 2017), coating the surface of Li$_4$Ti$_5$O$_{12}$ particles with conductive materials...
construction of nanoscale particle size (Chiu et al., 2017), and introduction of metal and nonmetal ion into Li$_4$Ti$_5$O$_{12}$ (Chen et al., 2017; Cheng et al., 2017; Liang et al., 2017).

Thin carbon coating on the surface of Li$_4$Ti$_5$O$_{12}$ particles has been considered as an effective method to enhance its electrochemical properties in all reported literatures, since the carbon coating can both improve the surface electron conductivity and inhibit the growth of primary particles in the heat treatment process, this further leads to faster lithium ion diffusion. Very recently, the introduction of nitrogen-doped carbon to modify the electrode materials has been received more and more attention. It is well-known that N atoms can provide additional electrons to further increase the conductivity of the coated carbon layer (Jiang et al., 2017; Xu et al., 2017). In addition, N-doped is favorable to reduce the barrier of energy of lithium-ion penetration and enhance reaction sites (Xiong et al., 2018). We have just proposed folic acid as a new carbon precursor to prepare Li$_4$Ti$_5$O$_{12}$@CN composite. It is well-expected that the as-prepared Li$_4$Ti$_5$O$_{12}$@CN sample will possess excellent electrochemical characters.

**EXPERIMENTAL**

**Material Preparation**

Li$_4$Ti$_5$O$_{12}$@CN composite was synthesized via a solid-state process, and the detail process was described as following. Firstly, 2.2281 g of Li$_2$CO$_3$ (99.5%), 5.9985 g of TiO$_2$ (99.9%) and 1 g of folic acid were mixed by ball milling in ethyl alcohol for 6 h. Secondly, the solvent was evaporated by drying the ready-prepared mixture at 80°C for 2 h. Thirdly, the synthesized precursor was heated under argon atmosphere at 750°C for 8 h. For comparison, pure Li$_4$Ti$_5$O$_{12}$ was also synthesized via the similar method without using folic acid as the starting material.

**Characterization of Materials**

X-ray diffraction instrument was used to investigate the structure and composition of both as-prepared Li$_4$Ti$_5$O$_{12}$ samples. The surface chemical states of Li$_4$Ti$_5$O$_{12}$@CN were identified by XPS. SEM was used for observing morphologies of the two ready-prepared Li$_4$Ti$_5$O$_{12}$ samples. N-doped carbon layer was further investigated by TEM. Elemental analyzer was carried out to investigate the content of carbon and nitrogen for Li$_4$Ti$_5$O$_{12}$@CN composite. Four-point probe method was used to investigate the electronic conductivities of both Li$_4$Ti$_5$O$_{12}$ samples.

**Electrochemical Measurements**

The fabricated working electrodes consisted of as-synthesized Li$_4$Ti$_5$O$_{12}$ sample, LA-132 and Super-P in a weight ratio of 85:5:10. The mixture was uniformly casted onto the aluminum foil and then dried in vacuum. CR2032 coin type cells were prepared in glove box with filled argon by composing of lithium piece as the counter electrode, 1 mol/L LiPF$_6$ in EC/DEC/DMC (1:1:1 in volume) as the electrolyte. Celgard 2400 as the separator. LAND CT2001 system were used to investigate the charge-discharge experiments between the potential range of 1–3V. Electrochemical impedance spectra (EIS) were investigated by using CHI600E electrochemical station in a frequency range of $10^{-2}$–$10^5$ Hz.

**RESULTS AND DISCUSSION**

Crystal structure of both as-obtained Li$_4$Ti$_5$O$_{12}$ samples was characterized via XRD, and the results are plotted in Figure 1. It clearly verifies that the dominating diffraction peaks of both as-synthesized Li$_4$Ti$_5$O$_{12}$ samples are in consistence with the base peaks of spinel Li$_4$Ti$_5$O$_{12}$ (PDF No.49-0207), demonstrating that the nitrogen-doped carbon layer coating process has little effect on the formation of spinel Li$_4$Ti$_5$O$_{12}$ (Li et al., 2013a; Chang et al., 2014; Wang P. et al., 2017). Perhaps due to the amorphous morphology of carbon, the diffraction peak relative to carbon was not observed (Xu et al., 2017; Liu et al., 2018). The detail of the enlarged peak corresponding to Li$_4$Ti$_5$O$_{12}$ (111) plane was described in Figure 1B. As clearly found that the central position of this peak shifts to larger angles after N-doped carbon coating, suggesting that nitrogen atoms possibly doped into the Li$_4$Ti$_5$O$_{12}$ lattice and form a new thin layer of TiNx, similar phenomenon was also reported by Li et al. (Zhang et al., 2013). In addition, the intensity of the peaks in Li$_4$Ti$_5$O$_{12}$@CN composite is lower than that of pure Li$_4$Ti$_5$O$_{12}$, indicating that the N-doped carbon coating on the surface of Li$_4$Ti$_5$O$_{12}$ will prevent the growth of particles. In order to investigate the content of carbon and nitrogen in Li$_4$Ti$_5$O$_{12}$@CN composite, elemental analysis measurement is carried out. The content of carbon and nitrogen for Li$_4$Ti$_5$O$_{12}$@CN composite is 1.46 and 0.24%, respectively.

The obtained results of surface chemical state of Li$_4$Ti$_5$O$_{12}$@CN composite evaluated by X-ray photoelectron spectroscopy (XPS) are given in Figure 2. Li1s, Ti2p, O1s, C1s, and N1s peaks are observed from the XPS spectra of Li$_4$Ti$_5$O$_{12}$@CN composite (Figure 2A). The high-resolution N1s of Li$_4$Ti$_5$O$_{12}$@CN composite is demonstrated in Figure 2B. As illustrated in Figure 2B, pyridine (N1), pyrrole (N2) and graphitic (N3) correspond to peaks centered at 398.2, 399.8, and 401.4eV, respectively. (Li H. et al., 2014; Long et al., 2015; Wang et al., 2015). The above results clearly showed that nitrogen-doping is successfully introduced in the carbon layer by using folic acid as a carbon-nitrogen precursor, which might result in produce the flaws in the symmetric offset spread of aromatic rings carbon, and thus further increase the diffusion of Li$^+$ in the interface (Li et al., 2013a; Wang et al., 2015). Additionally, a peak at about 397 eV being attributed to the interaction energy of TiN is observed in Figure 2B, indicating that titanium nitride (TiN) phase is created during the sintering process (Wan et al., 2012). As well-accepted, the existence of TiN with a metallic conductivity will improve electronic conductivity (Li H. et al., 2014). The high-resolution Ti2p of Li$_4$Ti$_5$O$_{12}$@CN composite is depicted in Figure 2C. Clearly, two peaks appeared at approximately 464.2 and 458.5eV are...
observed, which represents to peaks of Ti 2p1/2 and Ti 2p3/2 of Ti^{4+} in the sample (Li et al., 2014). In addition, two extra peaks located at about 459 and 464.7eV are detected, corresponding to the peaks of Ti 2p1/2 and Ti 2p3/2 of Ti^{3+} in the sample, respectively, which suggests that Ti^{3+} sites were introduced in the Li_{4}Ti_{5}O_{12}@CN composite due to the reduced ability of N-doped carbon. Similar phenomena were also demonstrated in previous reports (Wan et al., 2012; Ming et al., 2014). It further verified that the titanium nitride (TiN) phase was formed.

The different morphology and particle size between Li_{4}Ti_{5}O_{12} and Li_{4}Ti_{5}O_{12}@CN composites were investigated by SEM characterization. The results are shown in Figure 3. As clearly demonstrated in Figure 3, Li_{4}Ti_{5}O_{12}@CN composite possesses a much smaller particle size than that of Li_{4}Ti_{5}O_{12}. It is well-accepted that in situ N-doped carbon coating will well-prohibit the Li_{4}Ti_{5}O_{12} particles from growing into larger crystals (Wang C. et al., 2014). The SEM results agree well with the XRD results. To further verify this prediction, the specific surface area of both as-obtained Li_{4}Ti_{5}O_{12} and Li_{4}Ti_{5}O_{12}@CN samples were confirmed by four-point probe method. Pure Li_{4}Ti_{5}O_{12} and Li_{4}Ti_{5}O_{12}@CN composite have the electronic conductivities of $7.67 \times 10^{-5}$ and $1.06 \times 10^{-2}$ S cm$^{-1}$, respectively.

The first charge-discharge cycle for as-synthesized Li_{4}Ti_{5}O_{12} and Li_{4}Ti_{5}O_{12}@CN composite at a rate of 0.5 C between a voltage range of 1–3V are described in Figure 5. Both as-prepared Li_{4}Ti_{5}O_{12} samples possess a voltage plateau at ~1.55V, suggesting a two-phase reaction is carried out on the basis of the redox pair of Ti^{3+/4+} (Wang et al., 2012; Wang B. et al., 2014). However, the potential separation between the charge and discharge curves of Li_{4}Ti_{5}O_{12}@CN composite material is much smaller than that of Li_{4}Ti_{5}O_{12}, indicating that the Li_{4}Ti_{5}O_{12}@CN electrode has less polarization and better reaction kinetics, which
demonstrates that the enhancement of electrical conductivity of Li$_4$Ti$_5$O$_{12}$ after introducing N-doped carbon coating (Li et al., 2013a; Zhang et al., 2014).

The rate capabilities of Li$_4$Ti$_5$O$_{12}$@CN composite and Li$_4$Ti$_5$O$_{12}$ are shown in Figure 6. Pure Li$_4$Ti$_5$O$_{12}$ obtained a discharge capacity of 158 mAh g$^{-1}$ at a low rate of 0.5 C, and the capacity decreases remarkably as the rate increased from 0.5 to 1, 2, 5, and 10 C, respectively. Especially, its discharge capacity is only 79 mAh g$^{-1}$ at 10 C. The poor rate properties of pure Li$_4$Ti$_5$O$_{12}$ could be due to its poor conductivity. While much-improved discharge capacity at each rate for Li$_4$Ti$_5$O$_{12}$@CN composite in comparison with pure Li$_4$Ti$_5$O$_{12}$. At 0.5, 5, and 10 C, its discharge capacity were 174, 168, and 165 mAh g$^{-1}$, respectively. The superior rate properties of Li$_4$Ti$_5$O$_{12}$@CN composite could be due to three reasons: (i) As demonstrated in SEM results (See in Figure 4), the smaller particle size for Li$_4$Ti$_5$O$_{12}$@CN composite is favorable for the faster Li$^+$ diffusion and further enhancement of kinetic coefficient of lithium ion embedded into Li$_4$Ti$_5$O$_{12}$ structure (Long et al., 2015). (ii) The electronic conductivity of Li$_4$Ti$_5$O$_{12}$ is deemed to be enhanced by N-doped carbon coating (Xu et al., 2017), and the defects in the carbon layer caused by N-doping facilitate Li$^+$ migration in the interface (Li et al., 2013b). (iii) The electronic conductivity properties of Li$_4$Ti$_5$O$_{12}$ will be further increased with the existence of TiN$_x$ in the composite.

The cyclic property of Li$_4$Ti$_5$O$_{12}$@CN composite at a rate of 10 C is depicted in Figure 7. As clearly seen, the initial discharge capacity of Li$_4$Ti$_5$O$_{12}$@CN composite is 165 mAh g$^{-1}$, and 96.2% of its capacity is obtained after 200 cycles, suggesting that the as-synthesized Li$_4$Ti$_5$O$_{12}$@CN composite possesses good cycle stability.
To further investigate the effect of N-doped carbon coating on electrode behavior, electrochemical impedance spectroscopy measurements were performed on Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$@CN electrodes, and the results are plotted in Figure 8. Obviously, each electrode exhibits a similar profile with a straight line at the low frequency region and a depressed semicircle at the high-middle frequency range, being correlated with Li-ion diffusion and charges transfer resistance (Rct) in the electrode/electrolyte interface, respectively (Zheng et al., 2018; An et al., 2019; He et al., 2019; Lv et al., 2019; Xiao et al., 2019; Zhou et al., 2019). As obtained from Figure 8, Li$_4$Ti$_5$O$_{12}$@CN electrode exhibits much smaller charge-transfer resistance of 52 $\Omega$ than that of 194 $\Omega$ for pure Li$_4$Ti$_5$O$_{12}$ electrode, suggesting the improved electronic conductivity of Li$_4$Ti$_5$O$_{12}$@CN composite in comparison with pure Li$_4$Ti$_5$O$_{12}$ caused by the highly electronic conductive coating with N-doped carbon as well as the presence of TiN$_x$ phase (Zhou et al., 2017). According to the following equation, the Li-ion diffusion coefficient of both as-prepared Li$_4$Ti$_5$O$_{12}$ samples can be obtained:

$$D = \frac{R^2T^2}{2A^2n^4F^2C^2\sigma^2} \quad (1)$$

$$Z_{re} = R_D + R_L + \sigma\omega^{-1/2} \quad (2)$$

The value of $\sigma$ for both samples could be obtained from the lines described in Figure 9. Based on the above equations and the results from Figure 9, the obtained lithium ion diffusion coefficient for Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$@CN composite is $6.58 \times 10^{-11}$ and $2.89 \times 10^{-9}$ cm$^2$ s$^{-1}$, respectively. There is no doubt that the Li$_4$Ti$_5$O$_{12}$@CN electrode has a larger Li-ion diffusion coefficient due to the smaller particle size and the carbon layer defect of the Li$_4$Ti$_5$O$_{12}$@CN composite, indicating that a valid enhancement of the diffusion kinetics of Li$_4$Ti$_5$O$_{12}$ after the
introduction of the N-doped carbon coating. Based on the above results and discussion, coating with N-doped carbon can dramatically improve the lithium ion and conductive property. Consequently, Li$_4$Ti$_5$O$_{12}$@CN composite has much improved electrochemical performance in comparison with pure Li$_4$Ti$_5$O$_{12}$.

CONCLUSIONS

In this study, N-doped carbon-coated Li$_4$Ti$_5$O$_{12}$ is prepared with folic acid as a carbon-nitrogen source. Li$_4$Ti$_5$O$_{12}$@CN composite has the outstanding reversible capacity, high rate capability in comparison with pure Li$_4$Ti$_5$O$_{12}$. The discharge capacity of the Li$_4$Ti$_5$O$_{12}$@CN composite at 1 C was 165 mAh g$^{-1}$, and the initial specific capacity remained at 96.2% after 200 cycles. The superior properties of Li$_4$Ti$_5$O$_{12}$@CN composite could be owing to the improved electronic conductivity caused by the N-doped carbon layer and the TiN phase as well as enhanced Li-ion diffusion coefficient rising from the smaller particle size and the defects in the carbon layer.

REFERENCES

An, C. S., Yuan, Y. F., Zhang, B., Tang, L. B., Xiao, B., Lu, J., et al. (2019). Graphene wrapped Fe$_3$Se$_2$ nano-microspheres with high pseudocapacitive contribution for enhanced na-ion storage. Adv. Energy Mater. 2019:1900356. doi: 10.1002/aenm.201900356

Cheng, Q., Tang, S., Liu, C., Lan, Q., Zhao, J., Liang, J., et al. (2017). Preparation and electrochemical performance of Li$_4$Mg$_3$Ti$_5$O$_{12}$ as anode materials for lithium-ion battery. J. Alloy. Compd. 722, 229–234. doi: 10.1016/j.jallcom.2017.06.040

Chiu, H. C., Lu, X., Zhou, J., Gu, L., Reid, J., Gauvin, R., et al. (2017). Annealing-regulated elimination of residual strain-induced structural relaxation for stable high-power Li$_4$Ti$_5$O$_{12}$ nanosheet anodes. Nano Energy 32, 533–541. doi: 10.1016/j.nanoen.2016.12.063

Han, X., Gui, X., Yi, T. F., Li, Y. W., and Yue, C. B. (2018). Recent progress of NiCo$_2$O$_4$-based anodes for high-performance lithium-ion batteries. Curr. Opin. Solid State Mater. Sci. 22, 109–126. doi: 10.1016/j.cossms.2018.05.005

He, Z., Li, M., Li, Y., Li, C., Yi, Z., Zhu, J., et al. (2019). ZrO$_2$ nanoparticle embedded carbon nanofibers by electrospinning technique as advanced negative electrode materials for vanadium redox flow battery. Electrochim. Acta 306, 169–176. doi: 10.1016/j.electacta.2019.04.100

Jiang, C., Liu, S., Lian, Q., Zhao, J., Ding, W., Yu, Z., et al. (2017). Nitrogen-doped carbon-coated hierarchical Li$_4$Ti$_5$O$_{12}$-TiO$_2$ hybrid microspheres as excellent high rate anode of Li-ion battery. Ceram. Int. 43, 11354–11360. doi: 10.1016/j.ceramint.2017.05.341

Li, H., Shen, L., Zhang, X., Wang, J., Nie, P., Che, Q., et al. (2013a). Nitrogen-doped carbon coated Li$_4$Ti$_5$O$_{12}$ nanocomposite: superior anode materials for rechargeable lithium ion batteries. Power Sour. J. 221, 122–127. doi: 10.1016/j.jpowsour.2012.08.032

Li, R., Xiao, W., Miao, C., Fang, R., Wang, Z., and Zhang, M. (2019). Sphere-like SnO$_2$/TiO$_2$ composites as high-performance anodes for lithium ion batteries. Ceramics Int. 45, 13350–13355. doi: 10.1016/j.ceramint.2019.04.059

Li, X., Lin, H., Cui, W., Xiao, Q., and Zhao, J. (2014). Fast solution-combustion synthesis of nitrogen-modified Li$_4$Ti$_5$O$_{12}$ nanomaterials with improved electrochemical performance. ACS Appl. Mater. Interfaces 6, 7895–7901. doi: 10.1021/ams501220f

Long, D. H., Jeong, M. G., Lee, Y. S., Choi, W., Lee, J. K., Oh, I. H., et al. (2015). Synthesis and performance of Li$_4$Ti$_5$O$_{12}$ nanomaterials with improved electronic conductivity. Solid State Ionics 230, 113–117. doi: 10.1016/j.ssi.2018.02.035

Long, H. D., Jeong, M. G., Lee, Y. S., Choi, W., Lee, J. K., Oh, I. H., et al. (2015). Coating lithium titanate with nitrogen-doped carbon by simple refluxing for high-power lithium-ion batteries. ACS Appl. Mater. Interfaces 7, 10250–10257. doi: 10.1021/acsami.5b00776

Li, H., Shen, L., Zhang, X., Wang, J., Nie, P., Che, Q., et al. (2013b). Preparation of carbon nanosheet by molten salt route and its application in catalyzing VO$_2^{+}$/VO$_3^-$ redox reaction. J. Electrochem. Soc. 166, A953–A959. doi: 10.1149/2.037190jes

Ma, Z., Cui, Y., Xiao, X., Deng, Y., Song, X., Zuo, X., et al. (2016). A reconstructed graphite-like carbon micro/nano-structure with higher capacity and comparative voltage plateau of graphite. J. Mater. Chem. A 4, 11462–11471. doi: 10.1039/C6TA02195F

Xiao et al. Li$_4$Ti$_5$O$_{12}$@CN Composite

DATA AVAILABILITY

The raw data supporting the conclusions of this manuscript will be made available by the authors, without undue reservation, to any qualified researcher.

AUTHOR CONTRIBUTIONS

XH and YR contributed conception and design of the study. HX carried out experiments and wrote the manuscript. XD performed analyzed experimental results. SZ revised the manuscript.

FUNDING

This project was financially supported by the National Nature Science Foundation of China (Nos. 21771062, 21576030 and U1607127), the Research Fund of Hunan Provincial Education Department (18A366), the Opening Project of Material Corrosion and Protection Key Laboratory of Sichuan Province of China (No. 2018CI15).
performance in lithium-ion battery applications. *Electrochim. Acta* 116, 224–229. doi: 10.1016/j.electacta.2013.11.038

Tang, B., Li, A., Tong, Y., Song, H., Chen, X., Zhou, J., et al. (2017). Carbon-coated Li$_4$Ti$_5$O$_{12}$ tablets derived from metal-organic frameworks as anode material for lithium-ion batteries. *J. Alloy. Compd.* 708, 6–13. doi: 10.1016/j.jallcom.2017.02.279

Tian, Q., Chen, P., Zhang, Z., and Yang, L. (2017). Achievement of significantly improved lithium storage for novel clow-like Li$_4$Ti$_5$O$_{12}$ anode assembled by ultrafine nanowires. *Power Sour. J.* 350, 49–55. doi: 10.1016/j.jpowsour.2017.03.065

Wang, Z., Cai, R., Jiang, S., and Shao, Z. (2012). Nitrogen- and TiN-modified Li$_4$Ti$_5$O$_{12}$: one-step synthesis and electrochemical performance optimization. *J. Mater. Chem.* 22, 17773–17781. doi: 10.1039/c2jm33346e

Wang, B., Wang, J., Cao, J., Ge, H., and Tang, Y. (2014). Nitrogen-doped Li$_4$Ti$_5$O$_{12}$ nanosheets with enhanced lithium storage properties. *Power Sources J.* 266, 150–154. doi: 10.1016/j.jpowsour.2014.05.009

Wang, C., Li, H., Fu, A., Liu, J., Ye, W., Guo, P., et al. (2014). An RAPET approach to in situ synthesis of carbon modified Li$_4$Ti$_5$O$_{12}$ anode nanocrystals with improved conductivity. *N. Chem. J.* 38, 616–623. doi: 10.1039/C3NJ01319G

Wang, F., Luo, L., Du, J., Guo, L., Lia, B., and Ding, Y. (2015). Nitrogen-doped carbon decorated Li$_4$Ti$_5$O$_{12}$ composites as anode materials for high performance lithium-ion batteries. *RSC Adv.* 5, 46359–46365. doi: 10.1039/CSRA05989E

Wang, L., Zhang, Z., Liang, G., Ou, X., and Xu, Y. (2012). Synthesis and electrochemical performance of Li$_4$Ti$_5$O$_{12}$/C composite by a starch sol assisted method. *Powder Technol.* 215–216, 79–84. doi: 10.1016/j.powtec.2011.09.011

Wang, P., Zhang, G., Cheng, J., You, Y., Li, Y. K., Ding, C., et al. (2017). Facile Synthesis of Carbon-coated spinel Li$_4$Ti$_5$O$_{12}$/rutile-TiO$_2$ composites as an improved anode material in full lithium-ion batteries with LiFePO$_4$/N-doped carbon cathode. *ACS Appl. Mater. Interfaces* 9, 6138–6143. doi: 10.1021/acsami.6b15982

Wang, Q., Zhang, J., Liu, W., Xie, X., and Xia, B. (2017). Quantitative investigation of the gassing behavior in cylindrical Li$_4$Ti$_5$O$_{12}$ batteries. *Power Sour. J.* 345, 564–570. doi: 10.1016/j.jpowsour.2017.01.073

Wang, S., Yang, Y., Quan, W., Hong, Y., Zhang, Z., Tang, Z., et al. (2017). Ti$^{4+}$-free three-phase Li$_4$Ti$_5$O$_{12}$/TiO$_2$ for high-rate lithium-ion batteries: capacity and conductivity enhancement by phase boundaries. *Nano Energy* 32, 294–301. doi: 10.1016/j.nanoen.2016.12.052

Wu, L., Zheng, J., Wang, L., Xiong, X. H., Shao, Y. Y., Wu, M. H. et al. (2019). PPY-encapsulated SnS$_2$ nanosheets stabilized by defects on a TiO$_2$ support as a durable anode material for lithium-ion batteries. *Angew. Chem. Int. Ed.* 58, 811–815. doi: 10.1002/anie.201811784

Xiao, B., Wang, P. B., He, Z. J., Yang, Z., Tang, L. B., Zheng, J. C., et al. (2019). Effect of MgO and TiO$_2$ coating on the electrochemical performance of lithium-cathode materials for lithium-ion batteries. *Energy Technol.* 2019:1800829. doi: 10.1002/ente.201800829

Xiong, Q. Q., Lou, J. J., Teng, X. J., Lu, X. X., Liu, S. Y., Chi, H. Z., et al. (2018). Controllable synthesis of N-CoLiFePO$_4$ nanospheres as advanced cathode of lithium ion batteries. *J. Alloy. Compd.* 743, 377–382. doi: 10.1016/j.jallcom.2018.01.350

Xu, G., Quan, X., Gao, H., Li, J., Cai, Y., Cheng, X., et al. (2017). Facile spray drying route for large scale nitrogen-doped carbon-coated Li$_4$Ti$_5$O$_{12}$ anode material in lithium-ion batteries. *Solid State Ionics* 304, 40–45. doi: 10.1016/j.ssi.2017.03.018

Yi, T. F., Zhu, Y. R., Tao, W., Luo, S. H., Xie, Y., and Li, X. F. (2018). Recent advances in the research of MLi$_4$Ti$_5$O$_{12}$ (M=2Na, Sr, Ba, Pb) anode materials for Li-ion batteries. *Power Sour. J.* 399, 26–41. doi: 10.1016/j.jpowsour.2018.07.086

Zhang, H., Deng, Q., Mou, C., Huang, Z., Wang, Y., Zhou, A., et al. (2013). Surface structure and high-rate performance of spinel Li$_4$Ti$_5$O$_{12}$ coated with N-doped carbon as anode material for lithium-ion batteries. *Power Sour. J.* 239, 538–545. doi: 10.1016/j.jpowsour.2013.03.013

Zhang, T., Zhang, J., Peng, Z., Cai, W., Yu, L., Wu, Z., et al. (2014). Outstanding rate capability and long cycle stability induced by homogeneous distribution of nitrogen doped carbon and titanium nitride on the surface and in the bulk of spinel lithium titanate. *Electrochim. Acta* 132, 230–238. doi: 10.1016/j.electacta.2014.03.007

Zheng, J. C., Yang, Z., He, Z. J., Tong, H., Yu, W. J., and Zhang, J. F. (2018). In situ formed LiNi$_{0.8}$Co$_{0.1}$Al$_{0.1}$O$_2$/Li$_4$Ti$_5$O$_{12}$/rutile-TiO$_2$ composite cathode material with high rate capability and long cycling stability for lithium-ion batteries. *Nano Energy* 53, 613–621. doi: 10.1016/j.nanoen.2018.09.014

Zhou, C. X., Wang, P. B., Zhang, B., Tang, L. B., Tong, H. J., and Zheng, J. C. (2019). Formation and effect of residual lithium compounds on Li-rich cathode material Li$_{1.5}$[Ni$_{0.8}$Mn$_{0.2}$]O$_2$. *ACS Appl. Mater. Interfaces* 11, 11518–11523. doi: 10.1021/acsami.9b01806

Zhou, K., Fan, X., Chen, W., Chen, F., Wei, X., Li, A., et al. (2017). Nitrogen-doped Li$_4$Ti$_5$O$_{12}$/carbon hybrids derived from inorganic polymer for fast lithium storage. *Electrochim. Acta* 247, 132–138. doi: 10.1016/j.electacta.2017.06.175

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2019 Xiao, Huang, Ren, Ding and Zhou. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.