Influence of Li fast ion conductive La$_{0.56}$Li$_{0.33}$TiO$_4$ modification on morphology and electrochemical performance of LiFePO$_4$/C microspheres

Hongbo Shu*, Manfang Chen, Aiwen Wang, Xiukang Yang, Yangsong Bai, Yongqiang Shen, Xianyou Wang
Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, School of Chemistry, Xiangtan University, Xiangtan 411105, China

Introduction
The olivine LiFePO$_4$ was regarded as the most promising candidate of cathode materials due to its long cycle life, excellent safety and so on. Unfortunately, the low tap density, poor electronic and ionic conductivity have hampered its extensive applications in industry. Extensive work have been introduced to overcome intrinsic shortcomings. One way is to synthesize spherical morphology material with high tap density. Another important approach is surface coating of LiFePO$_4$ with electronic conductive materials (such as carbon) to enhance electronic conductivity of LiFePO$_4$. While transferred electron in LiFePO$_4$ must be reciprocally compensated by extraction/insertion of Li$^+$ to keep the charge balance during the charging/discharging process. If the Li$^+$ diffusivity can not attain the requisite diffusivity of transferred electron, it will limit the transferred electron, leading to deteriorated performance [1]. Thus, it is necessary to seek for an ideal coating layer with both high Li$^+$ and electron conductivity. To our knowledge, there have been rarely reports on using La$_{0.56}$Li$_{0.33}$TiO$_4$ or La$_{0.56}$Li$_{0.33}$TiO$_4$ and C hybrid coating to modify LiFePO$_4$.

In the present work, we fabricate La$_{0.56}$Li$_{0.33}$TiO$_4$ and C hybrid coating LiFePO$_4$ microspheres. As shown in Scheme 1(b), the designed hybrid coating layer composing of excellent electronic conductive C and perfect fast Li ion conductive La$_{0.56}$Li$_{0.33}$TiO$_4$ can fast transport both electron and Li ion, rather than only transport electron via single C coating shown in Scheme 1(a), and thus evidently enhance the high rate capacity and cycling stability. Herein, we reported LiFePO$_4$/C-La$_{0.56}$Li$_{0.33}$TiO$_4$ microspheres via an ammonia assisted hydrothermal route [2-3]. The effect of the La$_{0.56}$Li$_{0.33}$TiO$_4$ modification with various contents on the morphology and electrochemical performance of LiFePO$_4$/C are investigated.

Results and Discussion
As TEM shown in Fig. 1(a), the surface of LiFePO$_4$ particles are deposited a coating layer composing of two distinctive morphologies, namely relatively dark nanoparticles and gray flocule. It found that the relatively dark nanoparticles is crystalline La$_{0.56}$Li$_{0.33}$TiO$_4$ and the gray flocule is amorphous carbon via HR-TEM results, respectively. Besides, the XRD patterns of LiFePO$_4$/C-La$_{0.56}$Li$_{0.33}$TiO$_4$ were further investigated by Rietveld refinements which are revealed in Fig. 1(b). It can be fund that the diffraction peaks of LiFePO$_4$/C-La$_{0.56}$Li$_{0.33}$TiO$_4$ at around 11.3°, 34.4° and 47.9° correspond to the characteristic peak of La$_{0.56}$Li$_{0.33}$TiO$_4$, suggesting that La$_{0.56}$Li$_{0.33}$TiO$_4$ exist in synthesized LiFePO$_4$/C-La$_{0.56}$Li$_{0.33}$TiO$_4$.

As exhibited in Fig. 2(a), it is found that the rate capability is remarkably improved via coating with La$_{0.56}$Li$_{0.33}$TiO$_4$. Especially, LiFePO$_4$/C-La$_{0.56}$Li$_{0.33}$TiO$_4$ exhibit the excellent rate capability. It delivers a discharge capacity of 155.5, 142.1, 105.8, 86.0 and 62.3 mAh/g at 1 C to 30 C, respectively. Fig. 2(b) display the cycling performance of samples at 10 C. It can be seen that the discharge capacity and cycling stability performance of LiFePO$_4$/C increase gradually with the La$_{0.56}$Li$_{0.33}$TiO$_4$ coating content up to 2 wt.%, and then slightly decrease. It probably maybe because that inappropriate La$_{0.56}$Li$_{0.33}$TiO$_4$ coating content (e.g. 2 wt.%) can effectively enhance Li ion transport, while excess La$_{0.56}$Li$_{0.33}$TiO$_4$ coating content (e.g. 3 wt.%) will partly effect the electron transport due to poor electron conductor for La$_{0.56}$Li$_{0.33}$TiO$_4$.

Conclusions
The spherical LiFePO$_4$/C-La$_{0.56}$Li$_{0.33}$TiO$_4$ with various La$_{0.56}$Li$_{0.33}$TiO$_4$ contents are successfully synthesized by an ammonia assisted hydrothermal method. The surface of spherical LiFePO$_4$ is synchronously coated by C and La$_{0.56}$Li$_{0.33}$TiO$_4$, which can accelerate the electron and Li ion transport, and thus improve the electrochemical performance. Particularly, LiFePO$_4$/La$_{0.56}$Li$_{0.33}$TiO$_4$ exhibits the excellent rate capability and cycling stability. Thus, hybrid coating with C and La$_{0.56}$Li$_{0.33}$TiO$_4$ is an effective way to obtain LiFePO$_4$ batteries for the application in high-rate lithium ion batteries.

Acknowledgements
This work was funded by the National Natural Science Foundation of China under project No. 20871101, No. 51272221 and No. 51302339, Science and Technology plan Foundation of Hunan Province under project No. 2013FJ0462 and Universities in Hunan Province plans to graduate research and innovation under project No. CX2011B268.

References