The Improvement of Discharge Capacity of Zr-doped Lithium Titanate for Lithium Ion Batteries

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Abstract. $Li_4Ti_{5-x}Zr_xO_{12}$ ($0 \ll x \ll 0.05$) materials are synthesized via one-step liquid method in this work. The morphology, elemental distribution and lithium storage performance of Zr-doped lithium titanate are systematic analyzed by field emitting scanning electron microscopy (FE-SEM, Hitachi S-4800), energy dispersive X-ray (EDS) and Land battery test system (LAND CT2001A) together with the pristine lithium titanate for comparison. The FE-SEM images show the uniform morphology and narrow particle size distribution of Zr-doped samples. The cycle performance measurements demonstrate that the $Li_4Ti_{4.97}Zr_{0.03}O_{12}$ electrode displays the best discharge capacities among the composites. It delivers the initial discharge capacities of 165.4 mAh/g and 152.9 mAh/g at 5C and 10C, and remains the values of 142.9 mAh/g and 127.4 mAh/g after 200 cycles. Furthermore, the charge and discharge curves exhibit that the Zr-doped composite presents smaller polarization than the pristine lithium titanate.
Keywords: Lithium titanate; Anode; zirconium

1 Introduction

In the past few years, Lithium ion batteries (LIBs) have been improved rapidly due to its high energy density, excellent cyclic stability and high safety.[1, 2] Spinel lithium titanate ($Li_4Ti_5O_{12}$, LTO) is one of important anode materials of LIBs. It has a pair of long and stable charge and discharge potential flats, and the discharge potential is about 1.55 V (vs Li/Li^+), which is above the reduction potential of common electrolyte so that can hinder the formation of solid electrolyte interface (SEI). And this high potential also avoids the lithium dendrite deposition on the surface of the anode material[3, 4]. In addition, LTO is an ideal “zero strain” material because of no change of its lattice parameters and volume during lithium ion insertion/extraction processes.[5] However, its poor electrical conductivity seriously restricts its large scale applications.[6] Many efforts have been done to develop LTO electrical conductivity. Among them, doping with metal ions or metallic oxide is an

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effective method.[7] To utilize a metallic ion with high oxidation as substitution into either the Li^+ tetrahedral 8a site or Ti^{4+} octahedral 16d site, the electronic conductivity can be improved[8]. In this work, zirconium element was chosen to introduce to spinel LTO by simple one step liquid synthesis method. The composite of Zr-doped, $Li_4Ti_{5-x}Zr_xO_{12}$ (x=0, 0.02, 0.03, 0.05) expresses high rate performance and long cycle life than pure LTO. When x=0.03, the composite achieves the best electrochemical performance.

2 Experiment

Material preparation

$Li_4Ti_{5-x}Zr_xO_{12}$ samples were synthesized by a simple one step liquid method. Initially, 12.8g of tetrabutyl titanate (TBT) and moderate zirconium n-butoxide were dispersed in 20 mL anhydrous ethanol at room temperature with stirring until it dissolved completely. And 12.3g lithium hydroxide monohydrate ($LiOH•H_2O$) was added into 13mL deionized water under stirring for 30 minutes. Then, mixed these two solutions by peristaltic pump (flow rate is about $300\mu l•min^{-1}$) accompanying with vigorous stirring. After the titration , a cream-like mixture was obtained and kept in a vacuum oven at 100℃for 24 hours to get precursor substance. Subsequently, the precursor product was calcined at the temperature of 800℃for 5 hours at a heating rate of $5℃•min^{-1}$ in air. The synthetic procedures for LTO phase were identical to the steps above except the additive of zirconium n-butoxide.

3 Results and Discussion

Fig. 1a-d show the scanning electron microscopy (SEM) images of Zr-doped and pristine LTO powders. It can be seen that the morphologies of all composites are similar, and the particle sizes is between 200 and 500 nm. Fig. 1e and 1f show the Energy dispersive X-ray (EDX) mapping of $Li_4Ti_{4.97}Zr_{0.03}O_{12}$ (x=0.03), and they provide the exact information about Ti and Zr two elements distribution within the composite.

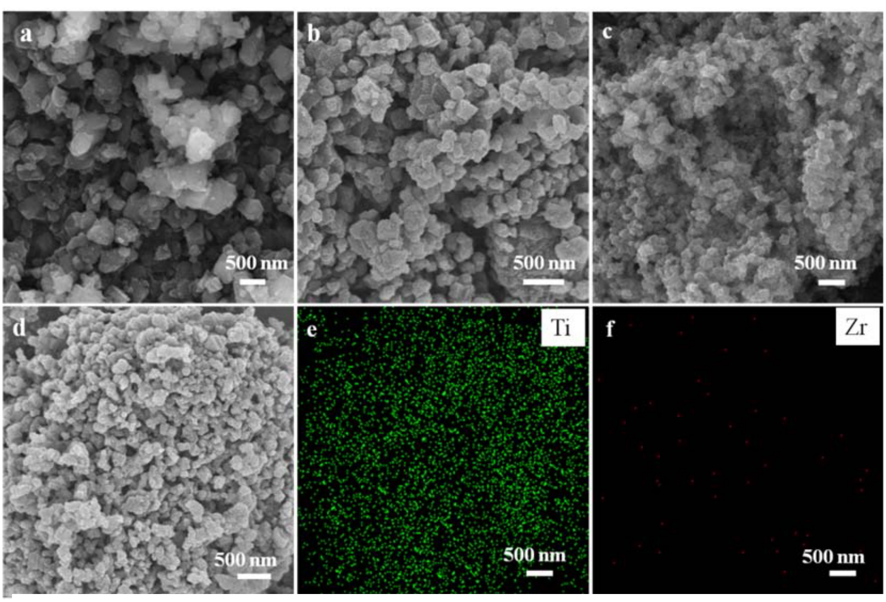

Fig. 1 SEM images of (a) pristine LTO, (b) $Li_4Ti_{4.98}Zr_{0.02}O_{12}$, (c) $Li_4Ti_{4.97}Zr_{0.03}O_{12}$, (d) $Li_4Ti_{4.95}Zr_{0.05}O_{12}$. The EDS mapping images (e, f) of

Fig. 2 displays the cycle performance of the pristine and Zr-doped LTO composites at different rates within the voltage range from 1.0 to 3.0 V. At 5C-rate, the initial discharge specific capacities of Zr-doped LTO (x=0.02, 0.03, 0.05) are 150.0 mAh/g, 165.4 mAh/g and 135 mAh/g, respectively. But the value of pure LTO is only 123.1 mAh/g. After 200 cycles, the retained capacities of Zr-doped LTO are 117.0 mAh/g, 142.9 mAh/g and 123.5 mAh/g, and the pristine sample is 102 mAh/g. The Zr-doped LTO exhibits more excellent discharge capacities. When at 10C-rate, the doped composites deliver discharge capacities of 138.0 mAh/g, 152.9 mAh/g and 128.9 mAh/g with x=0.02, 0.03 and 0.05. Meanwhile, at the 200th cycle thier retained capacities still reach 101.6 mAh/g, 127.4 mAh/g and 108 mAh/g, respectively. In contrast, the first and the 200th cycles capacities of the pure one are just 108.5 mAh/g and 84.2 mAh/g. All the coulombic efficiencies above are more than 99% except the initial cycle. Compared to the pristine, both the discharge specific capacity and the retention of the Zr-doped composites have been improved greatly at rate performance. And it is clear that the best one among them is $Li_4Ti_{4.97}Zr_{0.03}O_{12}$ (x=0.03). Fig. 2c shows the rate capability and cycling performance of $Li_4Ti_{4.97}Zr_{0.03}O_{12}$ (x=0.03). Even at high rate of 20C and 40C, the discharge capacity of the composite can reach 123.4 mAh/g and 118.0 mAh/g. The satisfactory lithium storage performance can be attributed to the improvement electrical conductivity of spinel LTO by Zr^{4+} doped.

Fig. 2d exhibits the initial cycle charge/discharge curves of Zr-doped and pure LTO electrodes at 10C-rate. All curves have very long and flat charge/discharge potential platforms. The potential difference of each pair charge and discharge potential platforms can be utilized to evaluate electrode polarization. The curves of the pure LTO have the biggest potential difference, which means the serious polarization among the electrodes. While the values of $Li_4Ti_{4.97}Zr_{0.03}O_{12}$ (x=0.03) and $Li_4Ti_{4.95}Zr_{0.05}O_{12}$ (x=0.05) are similar, and smaller than $Li_4Ti_{4.98}Zr_{0.02}O_{12}$ (x=0.02) lithely. It is evident that introduce Zr^{4+} to spinel LTO can decrease the electrode polarization during charge/discharge process.

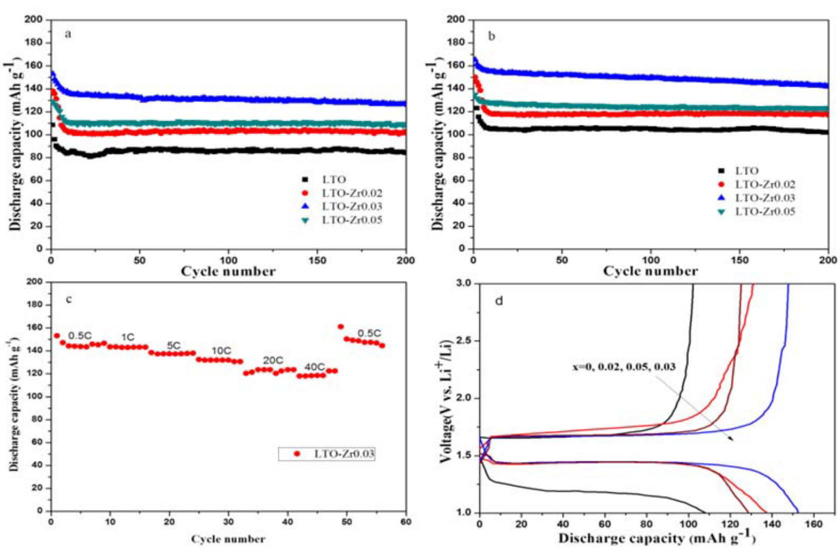

Fig. 2 Cycle performance of (a, b, c) $Li_4Ti_{5-x}Zr_xO_{12}$ ($0 \ll x \ll 0.05$), (c) rate performance of $Li_4Ti_{4.97}Zr_{0.03}O_{12}$, (d) the initial cycle galvanostatic discharge/charge voltage profiles of $Li_4Ti_{5-x}Zr_xO_{12}$ ($0 \ll x \ll 0.05$) at 10C.

4 Conclusion

One step liquid synthesis method is utilized to prepare $Li_4Ti_{5-x}Zr_xO_{12}$ ($0 \ll x \ll 0.05$), and the suitable amount of Zr-doped into LTO is x=0.03. The $Li_4Ti_{4.97}Zr_{0.03}O_{12}$ electrode exhibits the initial discharge capacities of 165.4 mAh/g and 152.9 mAh/g at 5C and 10C. After 200 cycles the retained capacities are 142.9 mAh/g and 127.4 mAh/g, respectively. In addition, the polarizations of Zr-doped samples are smaller than pristine LTO. In summary, Zr-doped procedure can improve the cycling performance and rate capacities of spinel LTO.

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