

Short Communication

Improving the Energy Density of Ca-Doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Through Discharging to 0 V Cut-off Voltage

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$\text{Li}_{3.9}\text{Ca}_{0.1}\text{Ti}_5\text{O}_{12}$ (LCTO) is synthesized by a solid-state reaction. X-ray diffraction (XRD) reveals that highly crystalline LCTO is obtained without any impurity. LCTO presents a higher discharge specific capacity and better cycling stability than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). LCTO exhibits a capacity of $240 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles at 1 C when discharged to 0 V, which is much higher than the LTO (only $127.3 \text{ mAh}\cdot\text{g}^{-1}$). The effect of Ca-doping on the improving the energy density of LTO discharged to 0 V was discussed. The electrochemical performances of LCTO and LTO in the voltage range from 0 to 2.5 V are also investigated.

Keywords: Lithium-ion batteries; $\text{Li}_4\text{Ti}_5\text{O}_{12}$; $\text{Li}_{3.9}\text{Ca}_{0.1}\text{Ti}_5\text{O}_{12}$; Anode materials; Doping; Energy density

1. INTRODUCTION

The spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been regarded as a promising anode material for lithium-ion batteries (LIBs) due to its outstanding characteristics, including zero volume change during charge-discharge process, high insertion potential of 1.55 V (vs. Li/Li^+) and low cost. In addition, LTO anode has a theoretical capacity of $175 \text{ mAh}\cdot\text{g}^{-1}$ within the voltage range of 1.0-2.5 V [1]. Unfortunately, LTO shows a low intrinsic electronic conductivity and Li^+ ion diffusion coefficient, resulting in poor high-rate performance [2]. Numerous ways have been exploited to improve the rate capability of LTO, such as surface coating [3-5], nanostructuring [6-7], doping [8-10], and hydrogen reduction [11]. Especially, doping has been proved to be an effective way to enhance the electronic conductivity. In our previous work, we proposed a facile way to synthesize a novel Ca-doped LTO, i.e., $\text{Li}_{3.9}\text{Ca}_{0.1}\text{Ti}_5\text{O}_{12}$ (LCTO), which exhibited better electrochemical performance than pure LTO due to its

improved electronic conductivity and lithium ion diffusivity when discharged to 1 V [12]. However, high energy density can be obtained by extending discharge voltage of the metallic ion doped-LTO to 0 V [13-14]. Thus, it is necessary to study the low discharge cut-off voltage behavior of LCTO with improved energy density. To our best knowledge, no related research work has been carried out. In this paper, we firstly reported the improved energy density of LCTO through discharging to 0 V cut-off voltage. The pristine LTO and doped LTO were synthesized by a simple solid-state reaction, and the structure, morphology, rate capability and electrochemical performance of LTO and LCTO discharged to 0 V was also investigated.

2. EXPERIMENTAL

Appropriate amounts of Li_2CO_3 , TiO_2 , CaO used as raw materials were mixed by ball milling for 8 h in acetone slurry, and then followed by drying at 100 °C for 4 h. Finally the products were calcined at 800 °C for 12 h in an air atmosphere to obtain the samples. 5% excessive Li was added to compensate for the Li volatilization during the high temperature heating process. The crystal structure of the as-prepared materials was identified by XRD using $\text{Cu-K}\alpha$ radiation ($10^\circ \leq 2\theta \leq 80^\circ$). SEM was used to investigate the particle size and morphologies of the as-prepared powders.

Electrochemical measurements were performed with CR2032 coin-type cells. The anodes were made of either the LTO and LCTO active materials with a carbon black conducting agent (Super P) and a polyvinylidene fluoride (PVDF) binder, with a weight ratio of 82:8:10. After these materials were thoroughly mixed in N-methyl-2-pyrrolidone (NMP) solution, the prepared slurry was coated on a copper foil using the doctor blade technique and dried at 120 °C in vacuum for 10 h to evaporate the NMP solvent. The electrode foil was punched to 12 mm diameter discs, which were used to assemble the coin cells in an argon-filled glove box where both moisture and oxygen content were less than 1 ppm. Li foil was used as the counter and reference electrode in the cell. Celgard 2400 was the separator. The electrolyte solution was 1 M LiPF_6 dissolved in a 1:1:1 mixture by volume of ethylene carbonate (EC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC). Charge-discharge cycling tests were performed at indicated current densities using a Land Battery Testing System. All the electrochemical tests were carried out at room temperature.

3. RESULTS AND DISCUSSION

The XRD patterns of LTO and LCTO are shown in Fig. 1(a). The diffraction peaks of both samples can be indexed as cubic spinel LTO. In our previous work, we have validated that the Ca^{2+} has successfully entered the lattice structure of LTO [12]. Nevertheless, after detailed examination of the enlarged XRD pattern as shown in Fig.1(b), the (1 1 1) peak of LCTO shifts to smaller angle, indicating that the LCTO has larger lattice constant than LTO, which is beneficial for fast lithium ion transfer without lattice stability damaged.

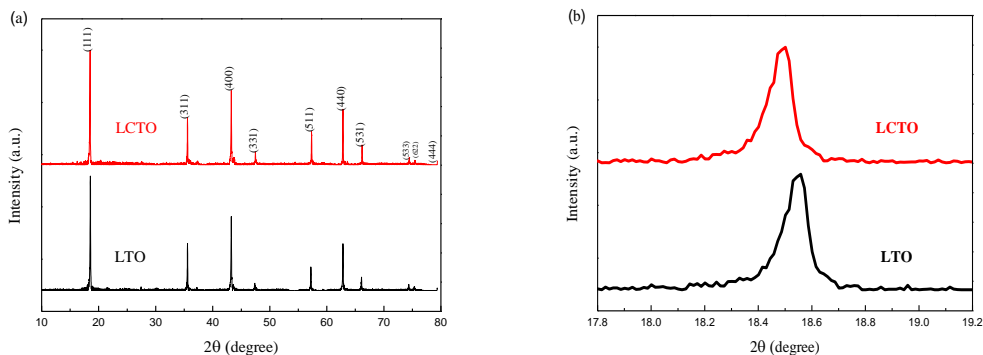


Figure 1. (a) XRD patterns and (b) magnified (1 1 1) peak of LTO and LCTO.

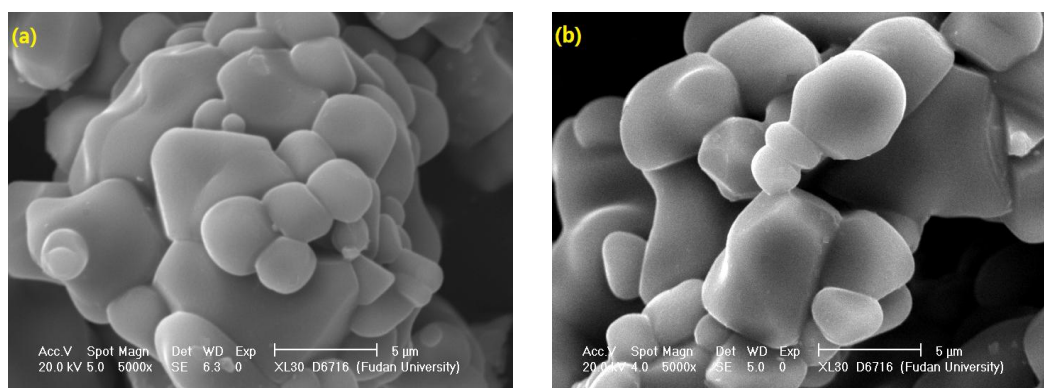


Figure 2. SEM images of (a) LTO and (b) LCTO

The powder morphology of the as-prepared LTO and LCTO is shown in Fig. 2. Both samples exhibit well crystallized with a particle size distribution in the range of 1-2 μm, but LCTO shows a relative small particle size and less agglomeration, which will be profitable to increase contact between grains and electrolyte, and then improve the discharge specific capacity.

The initial charge-discharge curves of LTO and LCTO discharge to 0 V at the current rate of 0.5 C, 1 C and 5 C are shown in Fig. 3. The discharge capacity decreases with the increasing current rates. However, the obvious capacity loss of LTO can be improved by doping Ca when discharged to 0 V. At the current rate of 0.5 C, 1 C and 5 C, LCTO presents an initial discharge capacity of 260.4 mAh·g⁻¹, 213.9 mAh·g⁻¹ and 184.8 mAh·g⁻¹, respectively. In contrast, LTO only has a discharge capacity of 242.7 mAh·g⁻¹, 169 mAh·g⁻¹ and 143.4 mAh·g⁻¹, respectively. Thus, it can be clearly seen that the LCTO higher discharge capacity than LTO when discharged to 0 V. The improvement in capacity can be attributed to Ca²⁺ doped into the lattice of LTO. Compared with LTO, the lattice constant of the LCTO is enlarged, which results in the broader path for lithium ion insertion and extraction.

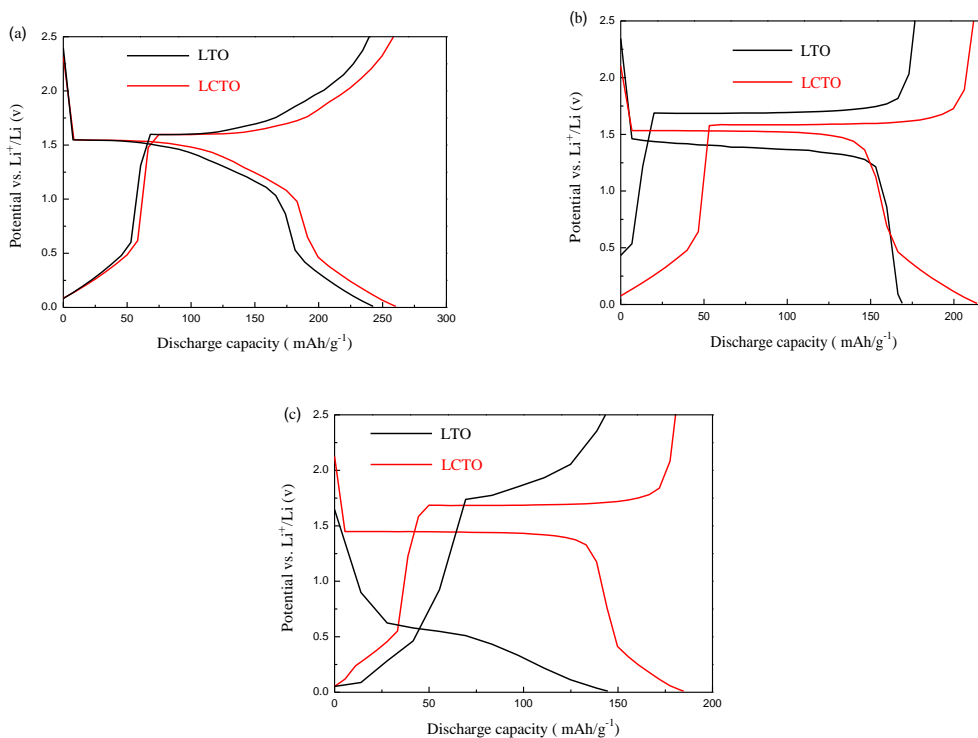


Figure 3. The initial charge-discharge curves of LTO and LCTO discharge to 0 V at the current rate of (a) 0.5 C, (b) 1 C and (c) 5 C.

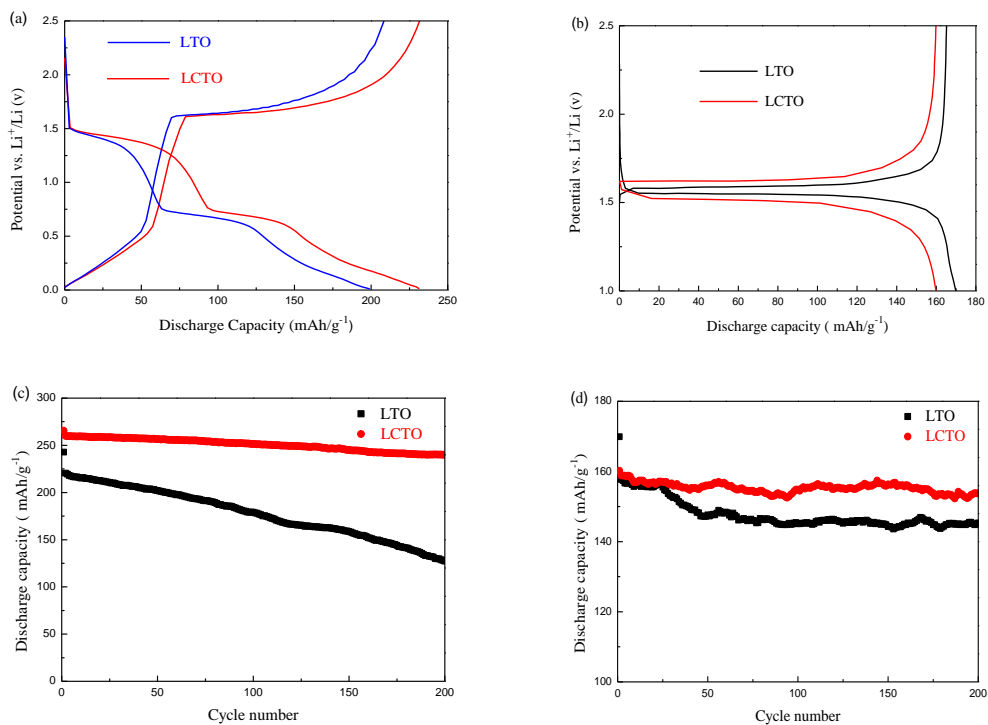


Figure 4. The 100th charge-discharge curves of LTO and LCTO discharges to (a) 0 V and (b) 1 V at 1 C rate. Cycling performance of LTO and LCTO discharged to (c) 0 V and (d) 1 V at 1 C rate for 200 cycles.

The 100th charge-discharge curves of LTO and LCTO electrodes down to 0 V are shown in Fig. 4(a) and (b). When cycled between 0 and 2.5 V, LCTO presents a discharge capacity of 231.3 mAh·g⁻¹ and reversible charge capacity of 230.7 mAh·g⁻¹, while LTO only has a discharge capacity of 199.1 mAh·g⁻¹ and a reversible charge capacity of 196.4 mAh·g⁻¹. Fig. 4c and d show the cycling performances of LTO and LCTO at the current rate of 1 C down to 0 V and 1 V. The LTO electrode shows a slightly higher initial capacity than LCTO due to the doping Ca ions which occupied Li 8a site. However, the 200th discharge capacity of LCTO down to 0 V is 240 mAh·g⁻¹, while the capacity of LTO is only 127.3 mAh·g⁻¹. When the cells are discharged to 1 C at the same current rate, the 200th discharge capacity of LCTO is 153.7 mAh·g⁻¹, while the corresponding value of LTO is 145.3 mAh·g⁻¹. The improvement of energy densities can be attributed to Ca²⁺ doping as discussed in our previous paper [12]. Obviously, when discharged to 0 V, the two samples have a big gap on the capacity and cycling performance. However, LTO discharged to 1 V at 1 C exhibits an obvious discharge plateau (Fig. 4b). In order to explain the different discharge plateau characteristic for LTO discharged to 0 V and 1 V at 1 C rate, the voltage versus time curve for LTO electrode cycled galvanostatically at 1 C in the range of 0-2.5 V is shown in Fig. 5(a), and the corresponding charge-discharge curve is shown in Fig. 5(b) as below.

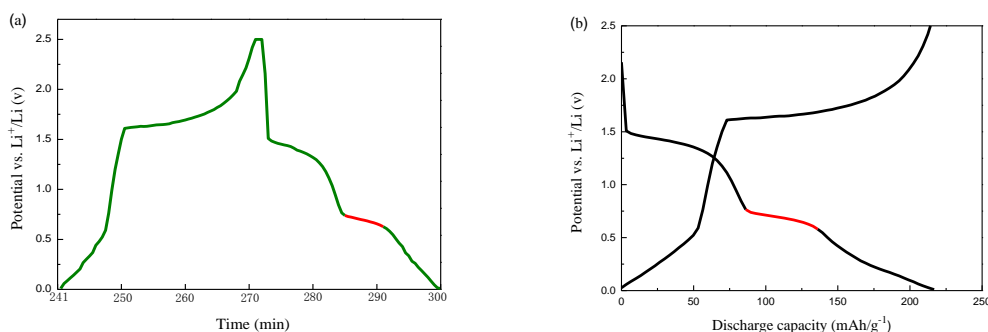
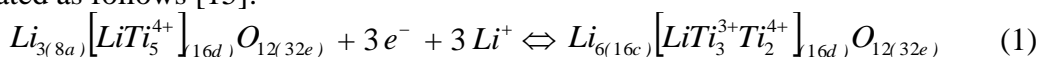
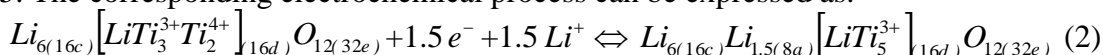


Figure 5. (a) the fifth electrochemical cycle of LTO and its corresponding charge-discharge curve (b).

It can be clearly seen from Fig. 5 that there are two flat plateaus in the voltage range of 1.0-2.5 V and below 1 V. The cycling behavior exhibits typical of LTO with a flat plateau around 1.55 V, which corresponds to the two-phase insertion reaction between Li₄Ti₅O₁₂ and Li₇Ti₅O₁₂, and can be formulated as follows [15]:



Three Ti⁴⁺ are reduced to Ti³⁺, accompanied by three lithium ions insertion into LTO. As the three Li ions occupy the octahedral (16c) sites of Li₇Ti₅O₁₂, there are still two Ti⁴⁺ remaining in Li₇Ti₅O₁₂. Thus, it is able to host more Li ions when cycled to a lower potential. Actually, on the basis of Zhong's research [16], Li₄Ti₅O₁₂ is transferred to Li_{8.5}Ti₅O₁₂ (but not Li₉Ti₅O₁₂, corresponding to full reduction from Ti⁴⁺ to Ti³⁺) when discharged to 0 V, which corresponds to a flat plateau below 1 V in Fig. 5. The corresponding electrochemical process can be expressed as:



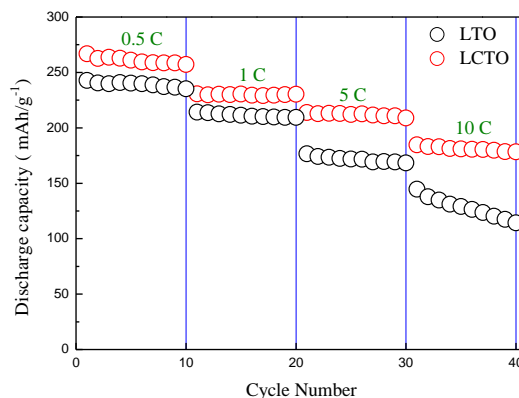


Figure 6. The cyclic performance of LTO and LCTO at various rates.

Fig. 6 displays the cyclic performance of LTO and LCTO cycled under different current rates vary from 0.5 C to 10 C and each for 10 cycles between the voltage limits of 0-2.5 V. Both electrodes present stable cycling performance at 0.5 C, 1 C and 5 C. However, the LTO electrode decreases almost linearly at 10 C rate and the capacity level of the LCTO is superior to it, manifesting the effective of the doping of Ca²⁺.

4. CONCLUSION

The powders of LTO and LCTO were successfully synthesized by a simple solid-state reaction. XRD patterns show that the LCTO has good crystallinity and high phase purity. Ca²⁺ doping enlarges the Li⁺ ion transport channel and is beneficial to the reversible insertion and extraction of Li⁺. The LCTO electrode presents a higher specific capacity and better cycling performance than the LTO electrode. LCTO has a capacity of 240 mAh·g⁻¹ at 1 C rate even after 200 cycles when discharged to 0 V. The LCTO anode exhibits a significantly improved rate capability compared to that of the pristine LTO. All the evidences demonstrate that Ca-doping is beneficial to the improvement of energy density of LTO discharged to 0 V. The LCTO electrode is expected to be a promising anode material for LIBs in future.

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References

1. Q.Y. Zhang and X. Li, *Int. J. Electrochem. Sci.*, 8 (2013) 6449.
2. S.H. Huang, Z.Y. Wen, X.J. Zhu and Z.H. Gu, *Electrochem. Commun.*, 6 (2004) 1093.

3. H.Y. Yu, X.F. Zhang, A.F. Jalbout, X.D. Yan, X.M. Pan and H.M. Xie, *Electrochim. Acta*, 53 (2008) 4200.
4. G.W. Xie, J.F. Ni, X.F. Liao and L.J. Gao, *Mater. Lett.*, 78 (2012) 177.
5. X.F. Guo, C.Y. Wang, M.M. Chen, J.Z. Wang and J.M. Zheng, *J. Power Sources*, 214 (2012) 107.
6. Y.S. Lin, M.C. Tsai and J.G. Duh, *J. Power Sources*, 214 (2012) 314.
7. H.F. Ni and L.Z. Fan, *J. Power Sources*, 214 (2012) 195.
8. Q.Y. Zhang and X. Li, *Int. J. Electrochem. Sci.*, 8 (2013) 7816.
9. B.B. Tian, H.F. Xiang, L. Zhang, Z. Li and H.H. Wang, *Electrochim. Acta*, 55 (2010) 5453.
10. Q.Y. Zhang and X. Li, *Int. J. Electrochem. Sci.*, 8 (2013) 6457.
11. R. Cai, S.M. Jiang, X. Yu, B.T. Zhao, H.T. Wang and Z.P. Shao, *J. Mater. Chem.*, 22 (2012) 8013.
12. Q.Y. Zhang, C.L. Zhang, B. Li, S.F. Kang, X. Li and Y.G. Wang, *Electrochim. Acta*, 98 (2013) 146.
13. T.F. Yi, Y. Xie, Q.J. Wu, H.P. Liu, L.J. Jiang, M.F. Ye and R.S. Zhu, *J. Power Sources*, 214 (2012) 220.
14. Y.R. Jhan and J.G. Duh, *Electrochim. Acta*, 63 (2012) 9.
15. G.N. Zhu, Y.G. Wang and Y.Y. Xia, *Energy Environ. Sci.*, 5 (2012) 6652.
16. Z.Y. Zhong, C.Y. Ouyang, S.Q. Shi and M.S. Lei, *Chemphyschem*, 9 (2008) 2104.