

Ultrasmall lithium titanate nanocrystals showing extremely fast lithium insertion

Dina Fattakhova-Rohlfing, Johann M. Feckl, Ksenia Fominykh, Markus Döblinger, Thomas Bein

Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU)
Butenandstr. 5-11 (E), 81377 Munich, Germany

The rapidly growing demand for electric vehicles and mobile electronics urgently requires the development of electrochemical energy storage systems with both high energy density and high power. Here we report the synthesis of mesoporous lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) thin films that feature a gravimetric capacity of about 175 mAh g^{-1} at rates of 1 – 50 C and can deliver up to 73 % of their maximum capacity at unprecedented high rates 400 C (Figure 1a) and up to 800 C (corresponding to 4.5 sec of charge/discharge) without deterioration up to several hundreds of cycles [1]. The pseudocapacitive storage contributes to about 55-60 % of the total charge, which can explain the unusually high rate performance of the developed LTO electrodes. This is the fastest ever reported titanate morphology for lithium insertion.

LTO is widely used as an active material in commercial lithium ion batteries and hybrid devices due to its suitable potential, relatively high capacity and robustness. Although the lithium insertion rate in bulk LTO is intrinsically low due to its low conductivity, recent reports have demonstrated that it can be substantially increased by decreasing the crystal size to the nanometer scale, and several approaches were developed to obtain nanoscaled material. In an effort to

reduce the crystal size even further, we have developed a solvothermal reaction in tert-butanol in the absence of water for the LTO synthesis [1], similar to the synthesis of ultrasmall titania nanocrystals reported by us earlier [2, 3]. In a reaction of appropriate molecular metal oxide precursors with tert-butanol, the spinel nuclei are formed already at a low reaction temperature of 170 °C. The formed nuclei are subsequently crystallized in a controlled way by a thermal treatment of the dried reaction mixture at 400 °C. The formed thin films of fully crystalline interconnected porous framework are composed of ultrasmall nanocrystals of only a few nm in size (Figure 1b). The high surface area of about $200 \text{ m}^2/\text{g}$ and the small crystal size allow for a very fast diffusion of the electrolyte inside the porous framework and short diffusion pathways inside the nanocrystals.

With this procedure we have created materials with properties typical for both batteries (high energy density) and for supercapacitors (high power densities). In combination with emerging fast nanostructured cathode materials, the ultrafast LTO anodes should have great potential for the development of Li-ion batteries that can operate both at high energy density and high power.

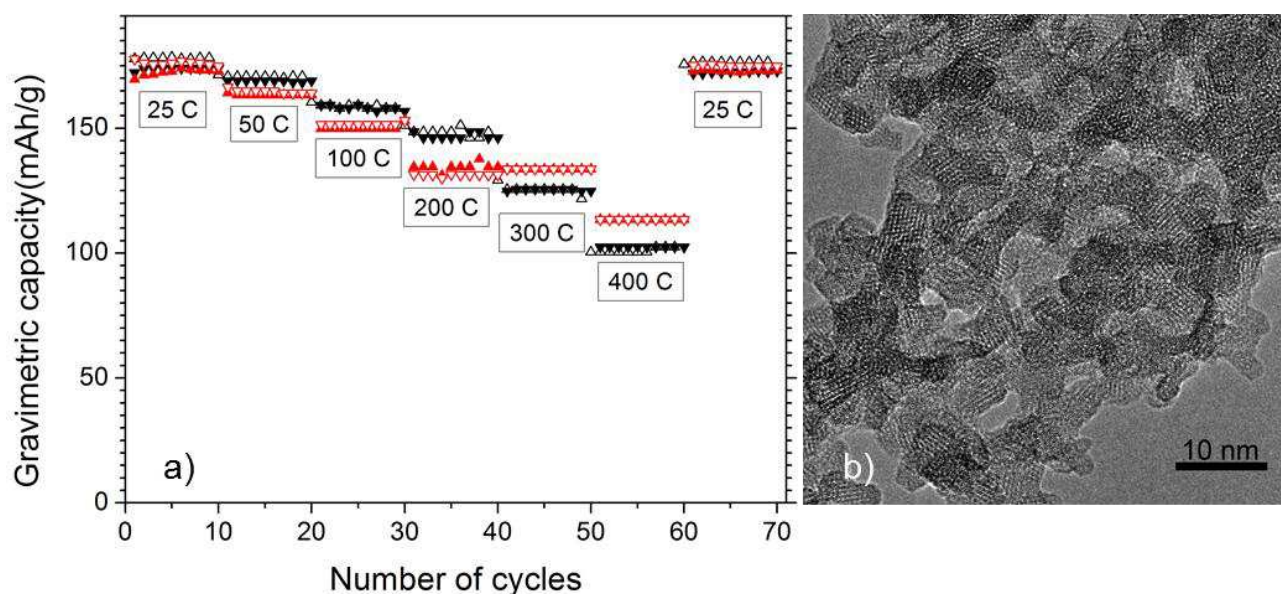


Figure 1. LTO spinel heated at 400 °C: TEM image (b) and multicycling stability at different rates during electrochemical Li insertion/extraction (a). The open and the filled symbols correspond to charge and discharge cycles, respectively. The cut-off potentials were 1 V and 2.4 V vs. Li. The thickness of the films is about $0.5 \mu\text{m}$ (corresponding to a loading of about 0.14 mg cm^{-2}). The measurements were performed in 1 M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ solution in a 1:1 by weight mixture of ethylenecarbonate and 1,2-dimethoxyethane using Li wires as both the auxiliary and the reference electrodes.

References

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