

Crystallized Lithium Titanate Nanosheets Prepared via Spark Plasma Sintering for Ultra-high Rate Lithium Ion Batteries

Junqin Li^a Tengfei Zhang,^a Cuiping Han,^{a,*} Hongfei Li,^b Ruiying Shi,^{c,d} Jing Tong,^{c,d} and Baohua Li^c

^a College of Materials Science and Engineering, Shenzhen University, and Shenzhen Key Laboratory of Special Functional Materials, Shenzhen 518060, China.

^b Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong 999077, China

^c Engineering Laboratory for Next Generation Power and Energy Storage Batteries, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

^d School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China

Corresponding authors: hancuiping06@szu.edu.cn (C. Han)

1. Experiment Section

1.1 Synthesis of LTO and LTO-SPS samples

LTO nanosheet precursor is prepared by hydrothermal reaction. In detail, 5.9 mL Tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, Sinopharm chemical reagent Co., Ltd, $\geq 98\%$) was slowly added into 60 mL cetyltrimethylammonium bromide (CTAB, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$, Sinopharm chemical reagent Co., Ltd, $\geq 99\%$) aqueous solution (13 g L^{-1}) under ultrasonic agitation. After fully hydrolysis, lithium hydroxide solution, prepared by dissolving 0.611 g lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$, Sinopharm chemical reagent Co., Ltd, $\geq 98\%$) in 20 mL purified water, was added into the above suspension. The mixture solution was then transferred into a 150 mL Teflon-lined stainless steel autoclave and treated at $180 \text{ }^\circ\text{C}$ for 24h. White precipitate was obtained after washing and drying at 90°C .

The LTO-SPS sample was prepared by calcination of the white precursor using SPS. In detail, the white precursor was loaded into the graphite die and was put into the SPS system. After evacuation, the sample was heated by pulse current to $500 \text{ }^\circ\text{C}$ for 5 min under a low axial pressure of about 5 MPa. Finally, the calcined sample is grounded by agate mortar to obtain the LTO-SPS powder. The LTO powder for comparison was prepared by conventional

calcination of the white precursor in tube furnace at 700°C for 2h in Ar filled atmosphere, which serves as a control.

1.2 Structural and electrochemical characterization

The phase composition was characterized by X-ray diffraction (XRD, Rigaku D/max 2500/PC using Cu K α radiation with $\lambda=1.5418\text{\AA}$). The morphologies and structures were examined on a field emission scanning electron microscopy (FE-SEM, HITACH S4800) at 5 kV and high resolution transmission electron microscope (HRTEM, TECNAI G2 F30) at an accelerating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) was conducted with a Physical Electronics PHI5802 instrument using an X-ray magnesium anode (monochromatic K α X-rays at 1253.6 eV) as the source. The C 1s region was used as a reference and was set at 284.8 eV.

All electrochemical measurements were carried out in a two electrode system using a CR2032-type coin cell. All cells were assembled in an Ar-filled glove box (Mbraum) with the prepared LTO and LTO-SPS as working electrodes, lithium foil as both counter and reference electrodes. The working electrodes were prepared by mixing 80wt% of the prepared active material (i.e. LTO and LTO-SPS), 10wt% acetylene black and 10wt% sodium alginate in deionized water to form a homogeneous slurry. The slurry was uniformly coated on a copper foil current collector and then dried in a vacuum oven at 110 °C for 10 h and pouched into disk-shaped electrodes with diameters of 12 mm. The mass loading of LTO and LTO-SPS is about 1.8~2.0 mg cm⁻². The tap density of LTO and LTO-SPS is 1.2 g/cm³ and 0.9 g/cm³, respectively.

Polypropylene membrane (Celgard 2500, Celgard Inc., USA) served as the separator. The electrolyte employed was a 1M LiPF₆ solution in ethylene carbonate (EC) / diethyl carbonate (DEC) / ethyl methyl carbonate (EMC) (volume ratio: 1:1:1). Cyclic voltammograms (CV) and electrochemical impedance spectrum (EIS) of cells were recorded with a VMP3 multichannel electrochemical working station. The CVs were performed within 1.0-2.5 V (vs. Li/Li⁺) at scanning rates of 0.1 mV s⁻¹, 0.2 mV s⁻¹, 0.5 mV s⁻¹, 1 mV s⁻¹ and 2 mV s⁻¹, respectively. The EISs were tested at half discharge state of electrode in the frequency range of 10⁻²-10⁵ Hz with a 5 mV perturbation. The assembled cells were also galvanostatically charged and discharged between 1.0 and 2.5 V (vs. Li/Li⁺) at different current densities using a Land 2001A battery testing system at 30 °C. 1C rate corresponds to a current density of 175 mA g⁻¹.

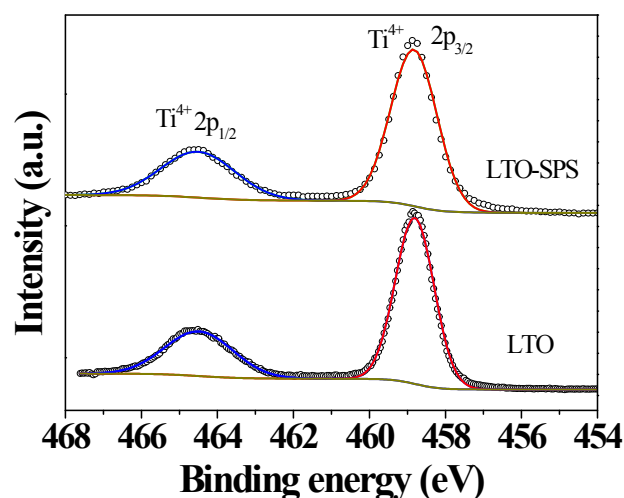


Figure S1. High resolution XPS spectra of Ti 2p for the LTO-SPS and LTO samples. The Ti 2p spectra in both samples display a spin-orbit doublet at binding energies of 458.8 eV for Ti 2p_{3/2} and 464.5 eV for Ti 2p_{1/2}, which is characteristics of Ti⁴⁺.

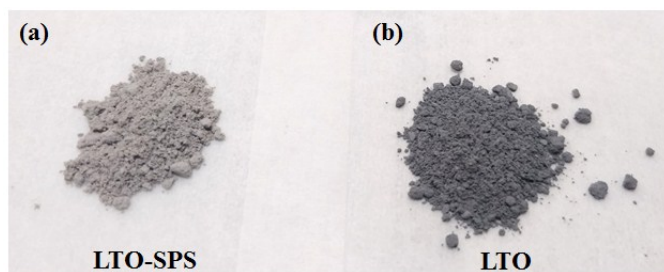


Figure S2. Photos of as-prepared (a) LTO-SPS and (b) LTO samples. The LTO-SPS presents a much light color than the LTO, suggesting that the carbon diffusion from the graphite mode to the powder is not obvious due to the low sintering temperature (500 °C) and short sintering time (5 mins). Note that the LTO shows a dark grey color due to small amount of residual carbon derived from the pyrolysis of surfactant added during the preparation.