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Formation mechanism of spinel $LiTi_2O_4$ prepared by carbon thermal reduction reaction

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Experimental

Materials

Li_2CO_3 (> 98%), anatase TiO_2 (> 99%) and acetylene black were purchased from Tianjin Fuchen Chemicals (China). The electrolyte (1 M $LiPF_6$ in ethyl carbonate/dimethyl carbonate (EC/DMC, v/v = 1:1, water content < 10 ppm)) was purchased from Guotai-Huarong New Chemical Materials Co. (China).

Synthesis and characterization of $LiTi_2O_4$

The spinel $LiTi_2O_4$ sample was synthesized by a one-step solid-state carbon thermal reduction reaction using Li_2CO_3 and TiO_2 as starting materials and acetylene black as a reducing agent. In a typical process, Li_2CO_3 (0.79 g, 5 mmol), anatase TiO_2 (3.22 g, 20 mmol) and acetylene black (0.06 g) were thoroughly mixed in agate mortar for 30 min. Then the mixture was calcined at 900 ℃ for 12 h in a tube furnace under nitrogen atmosphere, and subsequently cooled down to room temperature at a rate of 180 ℃ min^{-1}. $LiTi_2O_4$ with pure phase was obtained as a deep-blue powder.

The morphology of all the experimental samples was observed using a scanning electron microscope (SEM) (Hitachi S-4800, Japan). ^{7}Li MAS NMR spectrum of $LiTi_2O_4$ was acquired on an AV 400 Bruker spectrometer under magic angle sinning at 5 kHz using 4mm zirconium rotors. *In situ* VT-XRD was carried out on a PANalytical X'Pert Powder diffractometer with Cu Kα radiation (λ=1.5405Å), equipped with an Anton Parr HTK 1200N high temperature attachment. TA-SDTQ600 thermal gravimetric analysis/differential scanning calorimetry system was used to identify the phase transition temperature in N_2 atmosphere.

Measurements of electrochemical performances

The CR-2025 coin-type cells were assembled to test the electrochemical performance of the pure $LiTi_2O_4$. The $LiTi_2O_4$ electrode was prepared by mixing with active material, acetylene black and poly vinylidene fluoride (PVDF) at a weight ratio of 80: 10: 10 in a solution of N-methyl pyrrolidone (NMP) to form homogeneous slurry. The slurry was spread on a copper foil and dried at 110 °C for 24 h under vacuum. The CR-2025 coin-type cells were assembled in an Ar-filled glove-box using 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) solution as electrolyte. Celgard 2400 and lithium was used as separator and counter electrode, respectively. Galvanostatic charge/discharge tests were performed on a LAND CT2001A battery tester (China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopic (EIS) measurements were performed on an IM6e electrochemical workstation (Zahner, Germany). CV was conducted in cells at 0.2 mV s^{-1} from 0.8 V to 2.5 V. EIS was measured by applying an alternating voltage of 5 mV over the frequency ranging from 10^2 to 10^5 Hz.

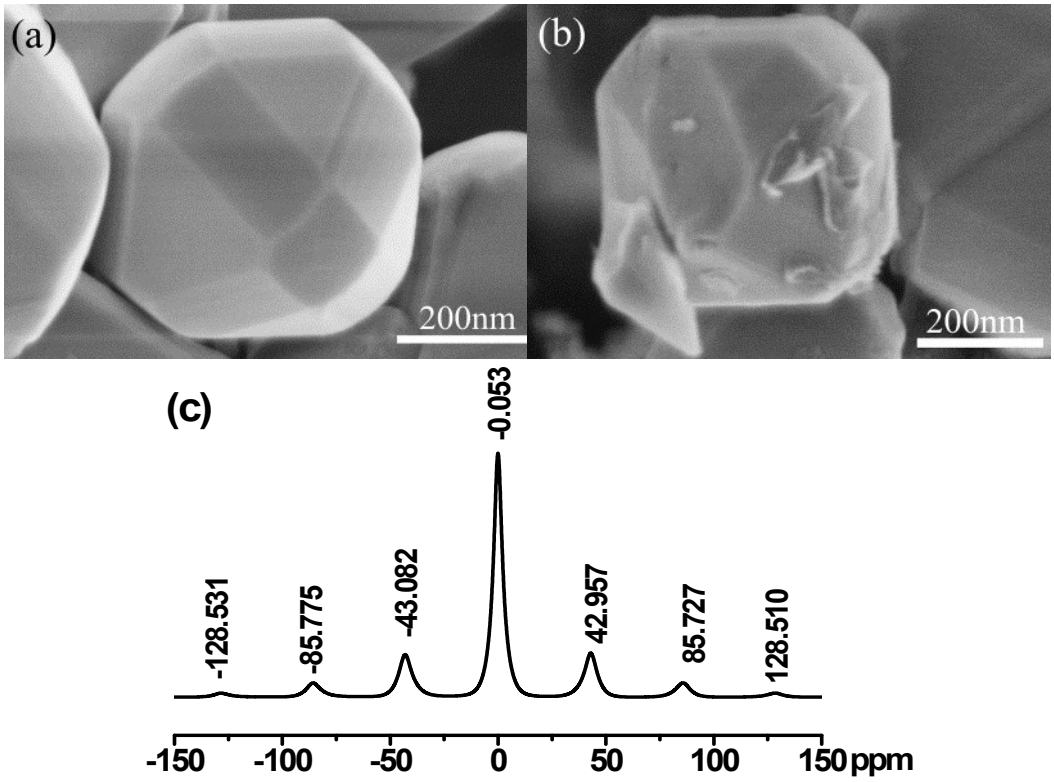

Figure S1. SEM images of $LiTi_2O_4$ during (a) 180℃ min^{-1} cooling rate and (b) 10℃ min^{-1} cooling rate and (c) ^7Li MAS NMR spectra of $LiTi_2O_4$ in 180℃ min^{-1} cooling rate with spinning speeds of 5 kHz.

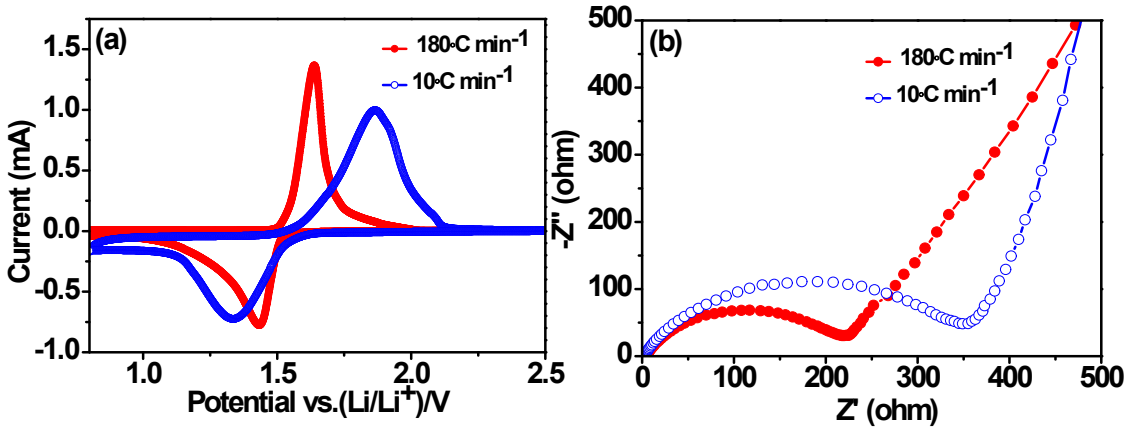

Figure S2. CV curves (a) and EIS plots (b) of $LiTi_2O_4$ electrode using the $LiTi_2O_4$ sample prepared at different cooling rate.

Table S1 Fitted results derived from EIS for $LiTi_2O_4$ at different cooling rates.

Sample	R_s (Ω)	R_{ct} (Ω)	CPE (μF)	i^0 (mA cm^{-2})
$LiTi_2O_4$-10	3.375	76.29	24.463	0.593
$LiTi_2O_4$-180	2.753	43.26	12.249	0.337