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Supporting Information

Structural transformations in Li_2MnSiO_4: A Li intercalation material can reversibly cycle through a disordered phase

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Experimental Section

***Materials preparation**:* Li_2MnSiO_4 was prepared through a chelating agent-assisted hydrothermal method as mentioned in our previous work.[1] In brief: 50 mmol $LiOH \cdot H_2O$ and 12.5 mmol SiO_2 were added into 20 ml distilled water and stirred for 10 min, then 2 g EDTA-4Na was added to form solution A. 10 ml $MnCl_2 \cdot 4H_2O$ solution with the concentration of 1.25 mol/L was poured into solution A and kept stirring for 30 min. the mixed solution was transferred to a 50 ml Teflon-lined stainless steel autoclave and heat at 170 °C for 48h. After naturally cooled, a layer of MnO_2 participate formed on the surface of the products was removed with a spatula, the remaining powder was washed by DI water and ethanol several times, then dried at 60°C.

For the synthesis of Li_2MnSiO_4@C composite, Li_2MnSiO_4 and glucose powder were mixed with a ratio of 4:3 by weight. The mixture was ground in agate mortar until uniformly mixed, then heat treated at 400°C for 1 h and 650°C for 10 h in an Ar atmosphere. The products were then cooled under ambient conditions.

Material characterization: X-ray diffraction (XRD) measurements were carried out with a Rigaku-Dmax 2500 diffractometer using Cu Kα radiation (λ=0.15405nm, 40 kV, 30 mA). The morphology was observed with a scanning electron microscope (SEM, FEI Quanta 200F)

Electrochemical measurements: Electrochemical performance was measured using CR2032 coin cells. For the fabrication of cathode materials, Li_2MnSiO_4@C composites, super P conductive carbon and poly (vinylidene fluoride) (PVDF) were mixed with a ratio of 7:2:1 by weight in N-methyl-2 pyrrolidone (NMP). The slurry was ground and spread onto aluminium foil, after which it was dried in a vacuum oven at 120 °C for 10 h. The typical loading of Li_2MnSiO_4@C composites is 1.2 – 2.4 mg cm^{-2}. The separator used was a Celgard M824 membrane; the counter and reference electrodes were lithium foils. The electrolyte, purchased from BASF, was composed of 1 M LiPF6 solution in ethylene carbonate (EC)/dimethyl carbonate (DMC) mixture solution (1:1 by volume). Galvanostatic charge/discharge tests were measured on a Land CT2001A battery test system (Land Wuhan Corp., China). All measurements were carried out at room temperature.

Ex-situ XRD measurements: For each ex-situ XRD measurement, the coin cells were transferred into a glove-box and dissembled immediately after cycling. The electrodes were washed with dimethyl carbonate several times to completely remove any residual electrolyte. The electrodes were stored in a glove-box until the XRD measurements were made.

Simulation of the Bragg peaks: The simulated Bragg peaks of the collapsed-$LiMnSiO_4$ and Li_2MnSiO_4 were carried out using the Full Proof software,[2] with the same Cu Kα radiation (λ=0.15405nm) as our XRD measurements.

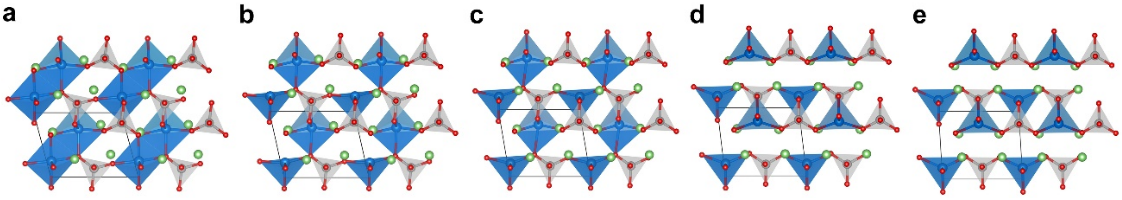

Figure S1. Intermediate structures along the minimum energy pathway of the structure recovery from collapsed Li_2MnSiO_4 to orthorhombic phase.

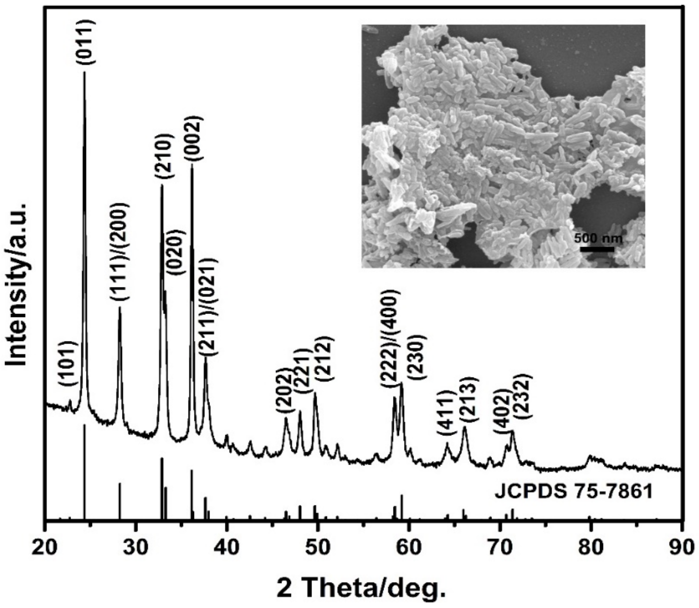

Figure S2 XRD pattern of Li_2MnSiO_4. Insert is the SEM image of carbon-coated Li_2MnSiO_4, the carbon content is 9%.

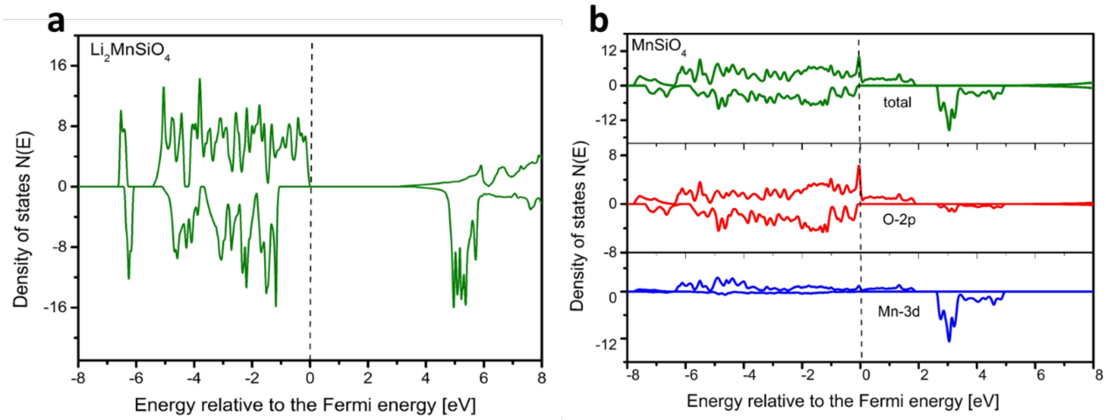

Figure S3. Calculated density of states of (a) Li_xMnSiO_4 (x=2, 0) and (b) $MnSiO_2$. The zero of the energy is set at the Fermi level.

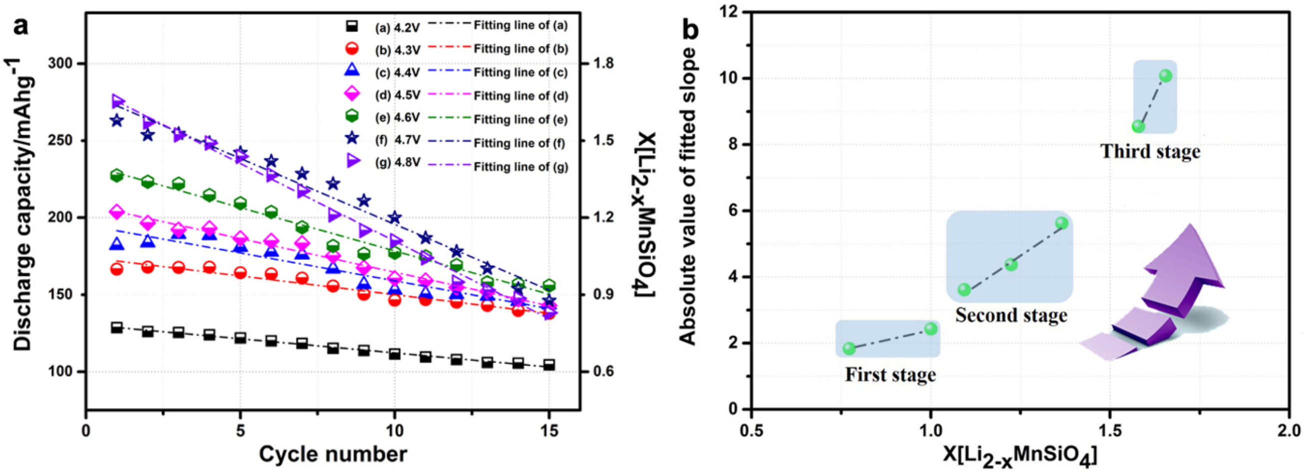

Figure S4 (a) Cycle performance and the linear trend lines of Li_2MnSiO_4. The electrodes were cycled between 1.5 -4.2 V, 1.5 -4.3 V, 1.5 -4.4 V, 1.5 -4.5 V, 1.5 -4.6 V, 1.5 -4.7 V, 1.5 -4.8 V, respectively. (b) The absolute value of the slope of the fitted curve in (a) as a function of lithiation state x in $Li_{2-x}MnSiO_4$. All the electrodes were tested at room temperature at a current set to 8.3 mA/g. The electrodes that were charged to higher voltage exhibit higher initial discharge capacity and more rapid capacity fade. To qualitatively determine the relationship of the capacity decay with state of charge, linear fits to the cyclic performance were carried out. Although not perfectly matched for each line, the fitted lines reflect the speed of capacity decay measured by the absolute value of slope of fitted curve as a function of lithiation state x in $Li_{2-x}MnSiO_4$. While not linear it is clear that the increase of the magnitude of the slope increases slightly for $1<x<1.5$, and significantly increased for $x>1.5$. That suggests that the capacity decay is faster upon extraction of more than 1 Li^+ per formula and then further aggravated with more Li extracted ($x>1.5$). In combination with our calculations, we suggest that the slight acceleration is caused by the collapse in $LiMnSiO_4$, which cumulatively introducing lattice strain inside the particles and causing structural instability; the subsequent aggravation is a result of the irreversible structure change arising from oxygen evolution.

References:

[1] Pei, Y.; Chen, Q.; Xu, C.; Wang, H.; Fang, H.; Zhou, C.; Zhen, L.; Cao, G., *J. Mater. Chem. A* **2016**, 4, 9447-9454.

[2] Rodríguez-Carvajal, *J. Phy. B: Condensed Matter* **1993**, 192, 55-69.