Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Materials

Effect of Sulfur Doping on Structural Reversibility and Cycling Stability of Li_2MnSiO_4 Cathode Material

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Figures:

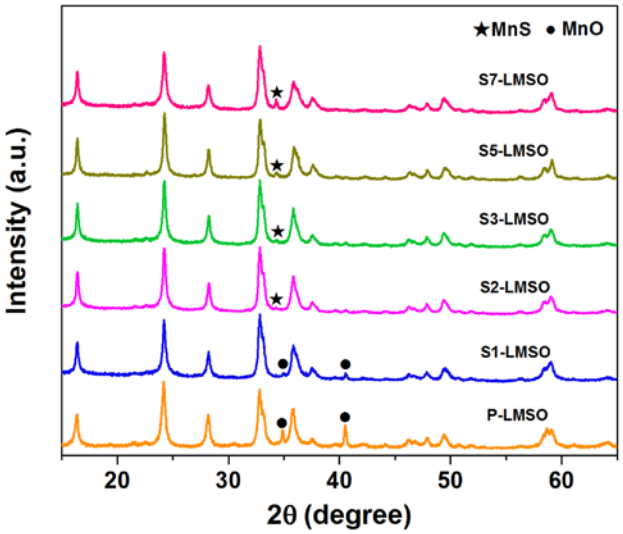

Fig. S1 The XRD patterns of $Li_2MnSiO_{4-x}S_x/C$ (x = 0, 0.01, 0.02, 0.03, 0.05 and 0.07) samples.

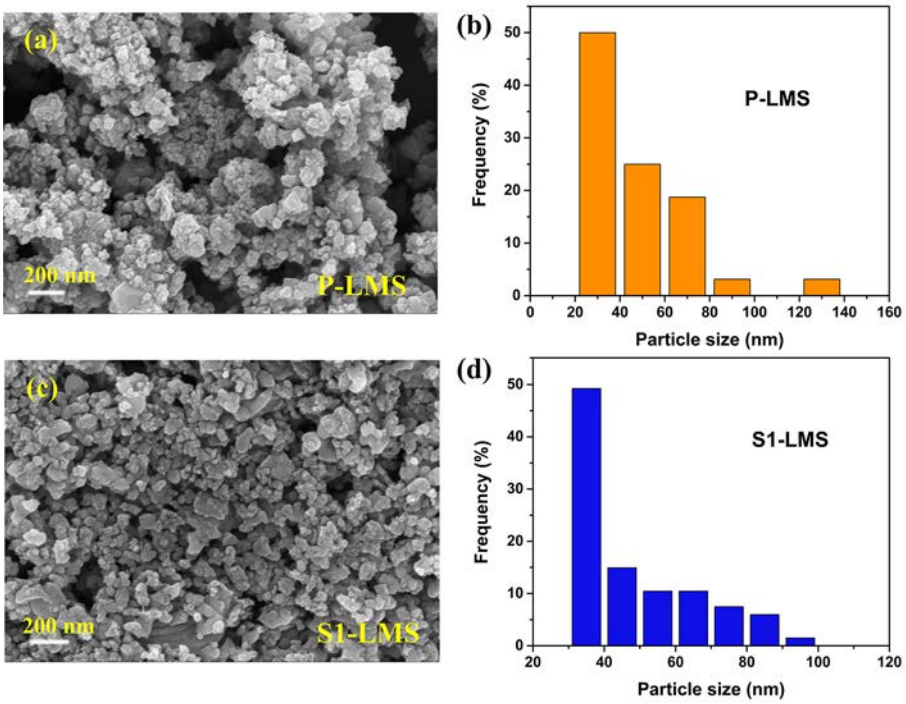

Fig. S2 SEM images of (a) P-LMS and (c) S1-LMS samples. The particle size distribution of (b) P-LMS and (d) S1-LMS samples.

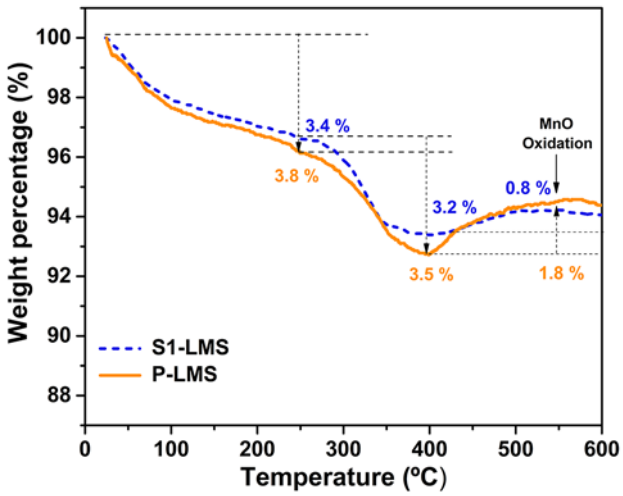

Fig. S3 TG curves of P-LMS and S1-LMS samples in the range of 50-600 °C at 10 /min rate in air.

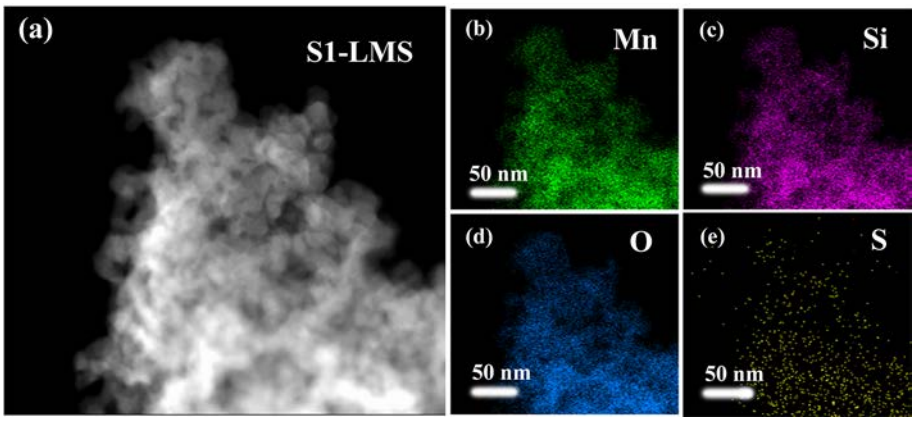

Fig. S4 HRTEM image (a) and elemental mapping (b-e) of S1-LMS sample.

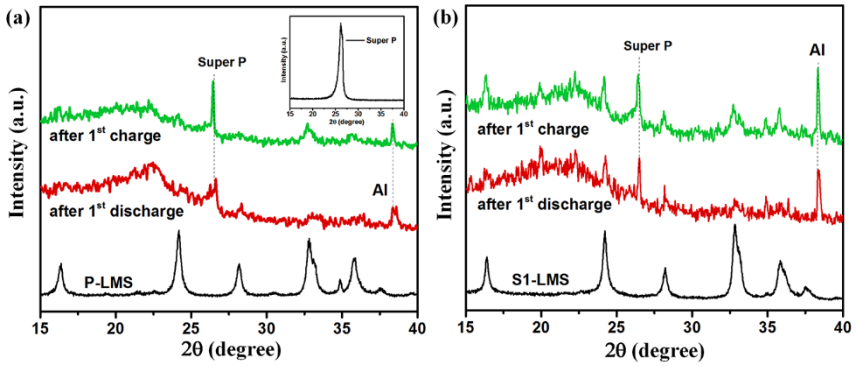

Fig. S5 *Ex-situ* XRD patterns of P-LMS and S1-LMS samples before and after first charge/discharge.

Table S1 I_D/I_G value of P-LMS and S1-LMS samples before/after cycling.

Samples	before cycle	after first charge	after first discharge
P-LMS	0.44	0.59	0.71
S1-LMS	0.42	0.56	0.66

The details of EIS fitting and calculation.

EIS was performed to explore the effect of S doping on reaction kinetic. The collected plots are consist of a semicircle in the high frequency region and a straight line in the low frequency region (Fig. 7c, d). The semicircle diameters are associated with the charge transfer resistance (R_{ct}) and the straight lines correspond to the lithium ion

diffusion process. The slope of the inclined line (insets) is Warburg factor (σ). The lithium ion diffusion coefficient (D_{Li+}) is calculated by following equation:

$$\mathrm{D} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma_w^2}$$

R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (298.15 K), A is the area of cathode electrode (0.95 cm^2 in our work), n is the number of electrons (2 in theory), F is the Faraday constant (96485 C·mol^{-1}), C is the molar concentration of lithium ion (0.0098 mol·cm^{-3}) and σ is the Warburg coefficient. The fitting results and calculations are displayed in Table 2.