Supplementary Information

Method

Synthesis of Li$_4$Mn$_5$O$_{12}$-like. We used a low-temperature solid-state synthesis method to prepare spinel Li$_4$Mn$_5$O$_{12}$-like samples. First, MnCO$_3$ (Aladdin, 99.95%) was mixed with LiOH·H$_2$O (Adamas, 99%). The molar ratio of MnCO$_3$: LiOH·H$_2$O was 5:4. After grounding for 1 h, the obtained mixture was sintered at 400°C for 12 h under air atmosphere to get the final material.

Material characterizations. X-ray diffraction was performed on Rigaku Ultima IV. It was operated in the 2θ value range of 10° to 80° with a 2°/min scanning rate. The morphology of Li$_4$Mn$_5$O$_{12}$-like sample was identified by Quanta 200 filed emission scanning electron microscope (FESEM). The HRTEM images were taken on a transmission electron microscope JEM-2100F with accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was carried out by use of ESCALAB 250Xi.

Electrochemical tests. CR2025-type coin cells, assembled in a glove box filled with dry argon gas, were used for electrochemical tests. A coin cell consisted of a positive electrode, an anode, ceramic membrane and organic electrolyte. To fabricate the positive electrode, active materials and carbon black (electron conduction) were ground with the weight ratio of 90:5. Then the as-prepared materials were mixed with polyvinylidene fluoride (PVDF) binder (95:5, weight ratio) in appropriate amount of N-methylpyrrolidone (NMP) using magnetic stirring to mix fully. The obtained slurry
was cast onto an aluminum foil current collector. Then, it was dried at 80°C overnight in vacuum. The organic electrolyte was 1mol/L LiPF₆ in a mixture of equal volumes of ethylene carbonate (EC) and dimethyl carbonate (DMC). For half cells and full cells, the anodes were lithium metal and lithium-tin alloy respectively. The electrochemical tests were carried out on a battery test system (Neware) between the voltage range of 1.8 V to 4.7 V (vs. Li⁺/Li) at different current density (0.1 C is equal to 25 mA g⁻¹). Electrochemical impedance spectroscopy (EIS) data was performed on a CHI600A Electrochemical workstation (Chinster, Shanghai, China), with 5mV ac excitation over a frequency range of 1 mHz to 100kHz. Cyclic voltammogram (CV) test was performed at a scan rate of 0.1 mV s⁻¹ among voltage range of 1.8 V to 4.7 V (vs. Li⁺/Li) by a CHI600A Electrochemical workstation (Chinster, Shanghai, China).

Result and discussion

In Fig. S1, cation- and anion-redox capacities evolving over cycles are examined individually, where an anion-redox capacity increment during the first 30 cycles was observed, probably due to an activation process of oxygen. In the subsequent cycles, a slow decline that might be related to oxygen release could be found. Meanwhile, cation-redox capacity deteriorates gradually with prolonged cycling, which is possibly attributed to the dissolution of manganese and the damage of structure.
Fig. S1. The cation- and anion-redox capacities evolving over cycles of Li$_4$Mn$_5$O$_{12}$-like cathode.

The tap density of well-prepared LMO cathode is about 3 g/cm$^3$. Therefore, the volumetric energy density of Li$_4$Mn$_5$O$_{12}$-like cathode is estimated to be as high as 2060 Wh/L. This value is quite competitive, compared to LFP and even NCM, but we believe it could be further optimized because at the present stage the primary particles is very small. And the volumetric energy density remains at 1450 Wh/L after 145 cycles.

![Graph showing volumetric energy density](image)

Fig. S2. Volumetric energy density of Li$_4$Mn$_5$O$_{12}$-like half cells from the 1$^{st}$ cycle to the 145$^{th}$ cycle at a current density of 100 mA g$^{-1}$ and a voltage window of 1.8 ~ 4.7 V versus Li$^+$/Li at room temperature.