Supporting Information

First-principles investigation on improved electron/ion transport and oxygen stability of Mo-doped Li$_2$MnO$_3$

Yurui Gao, a Jun Ma, a Xuefeng Wang, a Xia Lu, a Ying Bai, b Zhaoxiang Wang, *a and Liquan Chen a

a Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100190, China. *Email: zxwang@iphy.ac.cn Tel: +86-10-82649050 Fax: +86-10-82649050.

b Key Laboratory of Photovoltaic Materials of Henan Province and School of Physics and Electronics, Henan University, Kaifeng 475004, China

Materials Preparation and Characterization

Li$_2$MnO$_3$ and Mo-doped Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ ($x = 0.05, 0.10, 0.15, 0.20$) powders were synthesized by solid-state reaction with Li$_2$CO$_3$, MnCO$_3$ and MoO$_3$ as precursors at appropriate atomic ratios. To compensate for the possible Li loss during high temperature annealing, excess of
Li$_2$CO$_3$ (5 mol\%) was added. The precursors were mixed by milling in absolute ethyl ethanol and then annealed at 800 °C for 24 h in air. The structure of the obtained powders was characterized on an X’Pert Pro MPD X-ray diffractometer (XRD, Philips, Holland) with monochromatized Cu Kα radiation (λ = 1.5405 Å).

**Fig. S1** The primitive cell of Li$_2$MnO$_3$: (a) C2/m; (b) C2/c.

As the symmetry of C2/m is higher than that of C2/c, the primitive cell of m-Li$_2$MnO$_3$ is nearly half that of c-Li$_2$MnO$_3$.

**Fig. S2** XRD of the Li$_2$MnO$_3$ prepared by the solid-state reaction.
**Fig. S3** Ground state of Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ ($x = 1/16, 2/16, 3/16$ and $4/16$).

**Fig. S4** Band structures (spin up) of Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ ($x = 1/16, 2/16, 3/16$ and $4/16$) and the width of the forbidden gap against $x$.

Fig. S4 shows the band structure (spin up) of Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ and the width of forbidden gap.
Electron bands appear in the forbidden gap and the width of the forbidden gap decreases when Mo is doped. In addition, the number of the doping electron bands increases gradually as $x$ increases from 1/16 to 4/16, in agreement with the results of the DOS analysis (Fig. 2c). As a result, the conductivity is expected to be increased with Mo doping. This is supported with the color change of the home-prepared Mo-doped Li$_2$MnO$_3$.

As $m$-Li$_2$MnO$_3$ and $c$-Li$_2$MnO$_3$ show similar electronic structures while the home-prepared Li$_2$MnO$_3$ shows a C2/c phase (Fig. S2), $c$-Li$_2$MnO$_3$ is adopted as the mother body in the following Mo doping investigation.

**Fig. S5** Charge density on a plane through (a) one Mn atom, its nearest-neighbor O(1) and O(2) in Li$_2$MnO$_3$; (b) the Mo atom, its nearest-neighbor O(1) and O(2) in Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ ($x = 1/16$).
Fig. S5 shows the charge density on a plane through one Mn or Mo atom, its nearest neighbor O(I) and O(II) in Li$_2$MnO$_3$ and Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ ($x = 1/16$), respectively. The charge density difference between Li$_2$MnO$_3$ and Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ along the O(I)-O(II) and the O(I)-M (M = Mo, Mn) lines is shown in Fig. S6. Clearly there is more positive charge than negative charge along both lines, consistent with the Bader charge analysis.
Fig. S7 Diffusion pathways of Li$_{2}$Mn$_{1-x}$Mo$_{x}$O$_{3}$ at $x=0$ (Li$_{2}$MnO$_{3}$).
Fig. S8 Diffusion pathways of Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ at $x=1/16$. 
Fig. S9 Diffusion pathways of Li$_2$Mn$_{1-x}$Mo$_x$O$_3$ at $x=4/16$.

Electrical conductivity measurement

The electrical conductivity measurements for Li$_2$MnO$_3$ and Mo-doped Li$_2$MnO$_3$ ceramic disks were performed by the AC impedance spectroscopy using an impedance/gain-phase analyzer (SI 1260, Solartron Metrology) between 100 Hz and 1 MHz. For ceramic disks preparation, the Li$_2$MnO$_3$ and Mo-doped Li$_2$MnO$_3$ precursors were firstly synthesized using appropriate ratio of Li$_2$CO$_3$, MnCO$_3$ and MoO$_3$ by a solid state reaction at 550 °C for 4 h in air. Then, the obtained precursors were grinded and separately mixed with a small amount of polyvinyl alcohol (PVA) as binder and pressed into a disk shaped pellet with about 15 mm diameter and 1-2 mm thickness.
under a mono-axial pressure of 14 MPa. The ceramic disks were sintered at 800 °C for 24 h in air. Silver electrodes were printed on both surfaces and subsequently fired at 500 °C for 15 min before electrical conductivity measurements.

Fig. S10 (a) The ceramic disks of the pristine and 15% Mo-doped Li$_2$MnO$_3$. The above three are ceramic disks of the pristine Li$_2$MnO$_3$ and the bottom three are ceramic disks of Li$_2$Mn$_{0.85}$Mo$_{0.15}$O$_3$. (b) AC impedance spectroscopy for the pristine and Li$_2$Mn$_{0.85}$Mo$_{0.15}$O$_3$ at room temperature.

According to the equations

$$\rho_f = \frac{R_f S}{h}$$
\[ \sigma_T = \frac{1}{\rho_T} \]

The electrical conductivity \( \sigma \) can be obtained as follows:

For the pristine \( \text{Li}_2\text{MnO}_3 \),

\[ h_1 = 0.1204 \text{ cm} \]
\[ S_1 = 1.268520 \text{ cm}^2 \]
\[ \rho_1 = 1.74032 \times 10^7 \Omega \cdot \text{cm} \]
\[ \sigma_1 = 5.74607 \times 10^{-6} \text{ S/m} \]

For \( \text{Li}_2\text{Mn}_{0.85}\text{Mo}_{0.15}\text{O}_3 \),

\[ h_2 = 0.1424 \text{ cm} \]
\[ S_2 = 1.577528 \text{ cm}^2 \]
\[ \rho_2 = 4.91249 \times 10^6 \Omega \cdot \text{cm} \]
\[ \sigma_2 = 2.03563 \times 10^{-5} \text{ S/m} \]

**Fig. S11** Simulation of Li removal \( \text{Li}_2\text{Mn}_{0.75}\text{Mo}_{0.25}\text{O}_3 \) (the ground state structures of \( \text{Li}_y\text{Mn}_{0.75}\text{Mo}_{0.25}\text{O}_3 \) with \( y = 2, 1.75, 1.5, 1.25 \) and 1).

**Table S1.** Calculated volume change of \( \text{Li}_2\text{Mn}_{1-x}\text{Mo}_x\text{O}_3 \) (\( x = 1/16, 2/16, 3/16, 4/16 \)) by PBE+U
(U_{eff}=4.9, 6.3 eV for Mn and Mo respectively, or U_{eff}=4.9 eV for Mn while Mo without U calibration) method.

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<th>Mo content x</th>
<th>Volume (Å³ f.u.⁻¹)</th>
<th>Volume expansion (%)</th>
<th>Volume* (Å³ f.u.⁻¹)</th>
<th>Volume expansion* (%)</th>
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<td>51.873</td>
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Notes: * result of Mo without U calibration.