Supplemental Information

Fast and Stable Li Metal Anode Enabled by Mo$_6$S$_8$ Artificial Interphase with Super Li-ion Conductivity

Ke Lu $^a$, Siyuan Gao $^a$, Robert J. Dick $^b$, Zain Sattar $^a$ and Yingwen Cheng $^a,$*

$^a$Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115 United States

$^b$Department of Science, Trine University, Angola, IN 46703 United States

*E-mail: ycheng@niu.edu
**Materials and methods**

**Material Preparation of Cu$_2$Mo$_6$S$_8$/C.** In a typical procedure for synthesizing Cu$_2$Mo$_6$S$_8$/C, 1.2 g CuS, 1.8 g Mo, 3.0 g MoS$_2$ and 0.6 g graphite were added to a ball milling container inside a Ar-filled glove box. The container was transferred out of the glove box and was ball-milled with a high-energy mechanical milling (8000 M, SPEX SamplePrep, USA) for 6 hours. After this process, the powders were collected and transferred to a tube furnace. The tube furnace was heated to 1000 °C for 10 hours under the flow of 100 sccm Ar, and was then cooled to room temperature. The products were collected and analyzed, and were Cu$_2$Mo$_6$S$_8$/C. The Cu$_2$Mo$_6$S$_8$ particles were synthesized using identical procedure without adding graphite.

**Preparation of Mo$_6$S$_8$/C:** Mo$_6$S$_8$/C particles were prepared from Cu$_2$Mo$_6$S$_8$/C by acid leaching off Cu$^{2+}$. In a typical procedure, 3.0 g of the as-synthesized Cu$_2$Mo$_6$S$_8$/C powders were added to 50 ml 8.0 M HCl. The mixture was stirred at room temperature for 1 day and the powders were collected by centrifuge, washed repeatedly with water until pH neutral, and then dried under vacuum at 100°C.

**Materials characterizations**

The crystallinity of the synthesized powders was examined by a Rigaku MiniFlex X-ray diffractometer. The particle size and morphology were analyzed using a Tecnai G2 twin TEM. The SEM images were collected using a Tescan Vega II microscope and the EDX spectra were collected using a INCAx-act Analytical EDS detector (Oxford Instruments).

**Electrochemical measurements**

The Mo$_6$S$_8$/C artificial films for stabilizing Li metal were prepared by mixing Mo$_6$S$_8$ particles (with or without carbon, as discussed in the manuscript), super-P carbon powder and polytetrafluoroethylene (PTFE) at a weight ratio of 90:5:5 and dried at 70 °C overnight under vacuum. Ni-rich NCM-811 (LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$, supplied by Argonne National Laboratory) were used for constructing full-cell Li metal batteries. A piece of Mo$_6$S$_8$/C coated Li foil was used as the anode and the separator was Celgard membranes. 70 μl of 1.0 M LiPF$_6$ in EC/DMC (1:1 vol) was used as the electrolyte. The type 2025 coin cells were assembled inside an Ar-filled glove box (Mbraun LabStar). Cyclic voltammograms were measured using a CH Instruments electrochemical working station. Cycling and rate performance tests were conducted using constant current and constant voltage modes using Neware CT-4008 battery testers. All the prototype Li metal full batteries were tested between 2.7 and 4.3 V. When the voltage reached
4.3 V, a constant voltage charge process at 4.3 V was applied until the charge current decreased to the value determined by C/10 (1C = 1.5 mA/cm²). Electrochemical impedance measurements were conducted at room temperature using a Gamry Reference 600 Potentiostat with a frequency range of 0.02 Hz to 100 kHz at the open circuit potential.

Figure S 1: XRD pattern of Mo₆S₈ synthesized without adding carbon in the precursors.

Figure S 2: TEM images of Mo₆S₈ particles synthesized without addition of carbon. These particles have much bigger size compared with the particles synthesized with carbon.
Figure S 3: Performance of Mo₆S₈ particles for hosting Li-ions: a) cyclic voltammogram acquired at 0.1 mV/s; b-c) charge/discharge voltage profiles and specific capacities at different C-rates (1C = 122 mA/g); d) cyclic stability at 10 C for 500 cycles.
Figure S 4: Discharge voltage profile of the Mo₆S₈||Li batteries to 0 V. The capacity was used to estimate the value of x in LiₓMo₆S₈.

Figure S 5: (a) X-ray diffraction pattern of fully discharged Mo₆S₈ (to 0V vs. Li, Li₁₆Mo₆S₈). The overall profile of the peaks match with PDF#36-1325 (which is Li₃.₃Mo₆S₈) reasonably well, so we believe the overall structure of the Chevrel phase was pertained after complete lithiation. (b) XRD patterns of the Mo₆S₈ electrode at the discharge depths of 1.5 V (Li₄Mo₆S₈) and 0 V (Li₁₆Mo₆S₈). The inset shows the enlarged region of the XRD patterns. During the lithiation processes, a high lattice stability was observed. Moreover, a gradual peak shift from about 13.68 for Li₄Mo₆S₈ to approximately 13.55 for Li₁₆Mo₆S₈ was observed, indicating that the interlayer space was slightly enlarged by the insertion of guest cations.
Figure S 6: Equivalent circuit for modeling the electrochemical impedance spectrum acquired from symmetrical cell. $R_s$: electrolyte resistance; $Q$: constant phase elements; $R_{ct}$: charge transfer resistance at Li surface; $Z_w$: Warburg impedance

Figure S 7: The Mo$_6$S$_8$/C coated Li metal anode show substantially better cyclic stability compared with pristine Li anodes under symmetric cell configuration (testing at 1.0 mA/cm$^2$ and 1.0 mAh/cm$^2$ per cycle).
Figure S 8: Equivalent circuit for modeling the electrochemical impedance spectrum acquired from Li metal full cells coupled with NMC-811 cathodes. The parameters $R_s$, $R_{sei}$ and $R_{ct}$ represent the electrolyte resistance, solid electrolyte interface (SEI) resistance and the charge transfer resistance, respectively; $Q_1$ and $Q_2$ represent the constant phase elements; $Z_w$ represents the Warburg impedance.

Figure S 9: Additional post-mortem SEM images acquired from pristine Li metal anode after being cycled for 200 cycles with the NMC-811 cathodes in carbonate electrolyte.
Figure S 6: Additional post-mortem SEM images acquired from hybrid Li metal anode after being cycled for 200 cycles with the NMC-811 cathodes in carbonate electrolyte. The bright agglomerated particles are Mo$_6$S$_8$/C composites and the black colored substrate underneath is Li metal.

Figure S 11 : Voltage profiles of the initial lithiation process of Mo$_6$S$_8$/C electrode, the current density was 2 mA cm$^{-2}$. 
Figure S 7: SEM images of the interphase between Mo₆S₈/C layer and Li metal (a) before and (b) after the 200 cycle test.