

Supplemental Information

Fast and Stable Li Metal Anode Enabled by Mo₆S₈ Artificial Interphase with Super Li-ion Conductivity

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Materials and methods

Material Preparation of Cu₂Mo₆S₈/C. In a typical procedure for synthesizing Cu₂Mo₆S₈/C, 1.2 g CuS, 1.8 g Mo, 3.0 g MoS₂ 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 Cu₂Mo₆S₈/C. The Cu₂Mo₆S₈ particles were synthesized using identical procedure without adding graphite.

Preparation of Mo₆S₈/C: Mo₆S₈/C particles were prepared from Cu₂Mo₆S₈/C by acid leaching off Cu²⁺. In a typical procedure, 3.0 g of the as-synthesized Cu₂Mo₆S₈/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 Mo₆S₈/C artificial films for stabilizing Li metal were prepared by mixing Mo₆S₈ 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}O₂, supplied by Argonne National Laboratory) were used for constructing full-cell Li metal batteries. A piece of Mo₆S₈/C coated Li foil was used as the anode and the separator was Celgard membranes. 70 μl of 1.0 M LiPF₆ 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

4.3V, a constant voltage charge process at 4.3 V was applied until the charge current decreased to the value determined by $C/10$ ($1C = 1.5 \text{ mA/cm}^2$). 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.

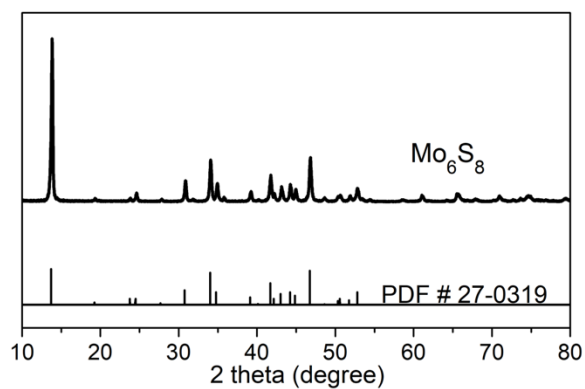


Figure S 1: XRD pattern of Mo_6S_8 synthesized without adding carbon in the precursors.

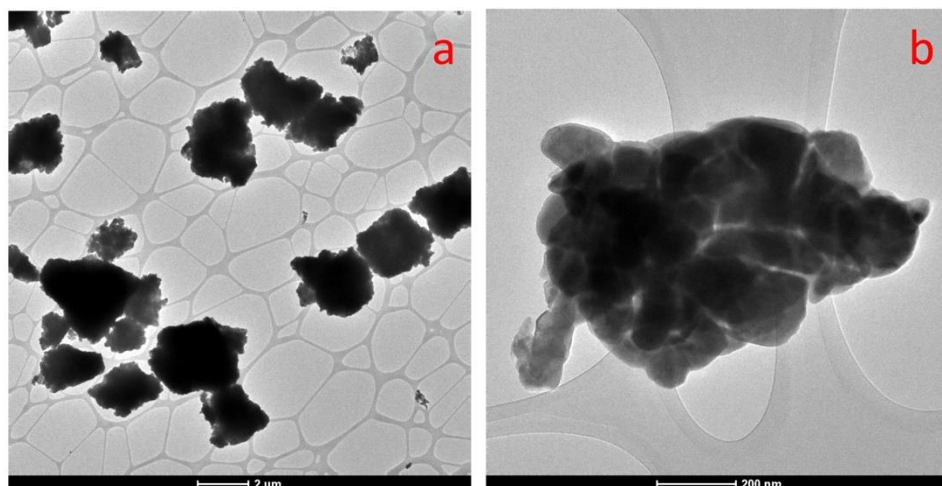


Figure S 2: TEM images of Mo_6S_8 particles synthesized without addition of carbon. These particles have much bigger size compared with the particles synthesized with carbon.

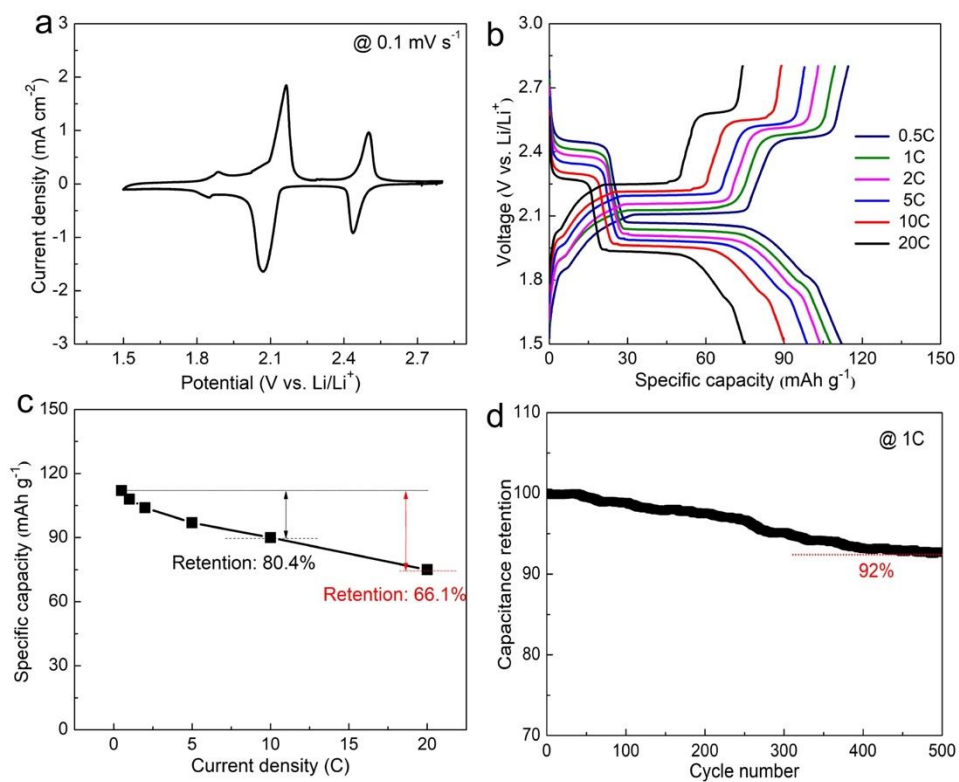


Figure S 3: Performance of Mo₆S₈ particles for hosting Li-ions: a) cyclic voltammogram acquired at 0.1 mV/s; b-c) charge/discharge voltage profiles and specific capacities at different C-rates (1C = 122 mA/g); d) cyclic stability at 10 C for 500 cycles.

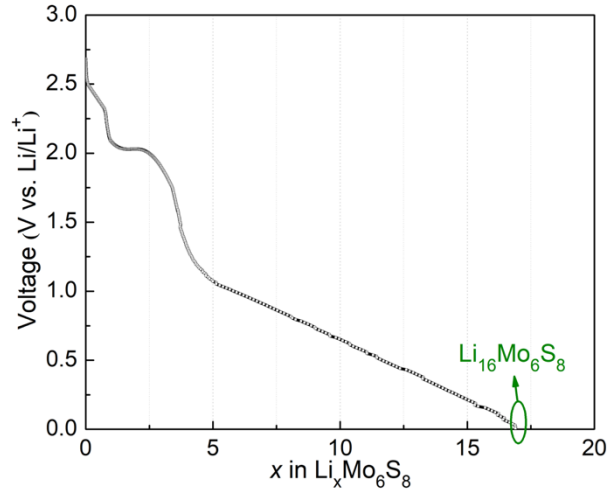


Figure S 4: Discharge voltage profile of the $\text{Mo}_6\text{S}_8\|\text{Li}$ batteries to 0 V. The capacity was used to estimate the value of x in $\text{Li}_x\text{Mo}_6\text{S}_8$.

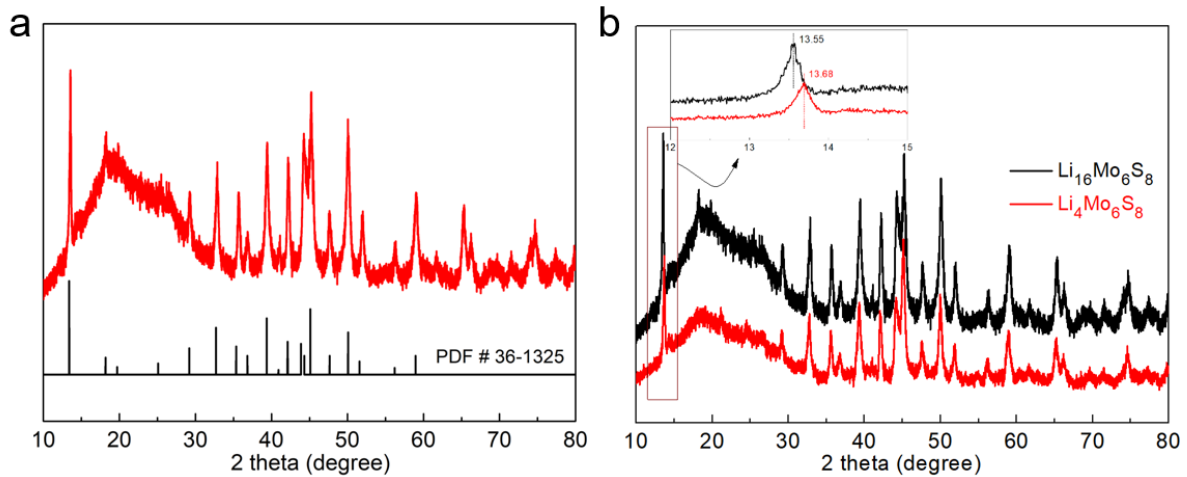


Figure S 5: (a) X-ray diffraction pattern of fully discharged Mo_6S_8 (to 0V vs. Li, $\text{Li}_{16}\text{Mo}_6\text{S}_8$). The overall profile of the peaks match with PDF#36-1325 (which is $\text{Li}_{3.3}\text{Mo}_6\text{S}_8$) reasonably well, so we believe the overall structure of the Chevrel phase was pertained after complete lithiation. (b) XRD patterns of the Mo_6S_8 electrode at the discharge depths of 1.5 V ($\text{Li}_4\text{Mo}_6\text{S}_8$) and 0 V ($\text{Li}_{16}\text{Mo}_6\text{S}_8$). 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 $\text{Li}_4\text{Mo}_6\text{S}_8$ to approximately 13.55 for $\text{Li}_{16}\text{Mo}_6\text{S}_8$ was observed, indicating that the interlayer space was slightly enlarged by the insertion of guest cations.

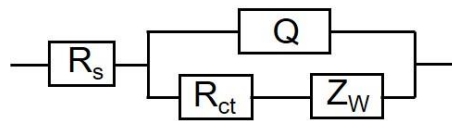


Figure S 6: Equivalent circuit for modeling the electrochemical impedance spectrum acquired from symmetrical cell. R_s : electrolyte resistance; Q : constant phase elements; R_{ct} : charge transfer resistance at Li surface; Z_w : Warburg impedance

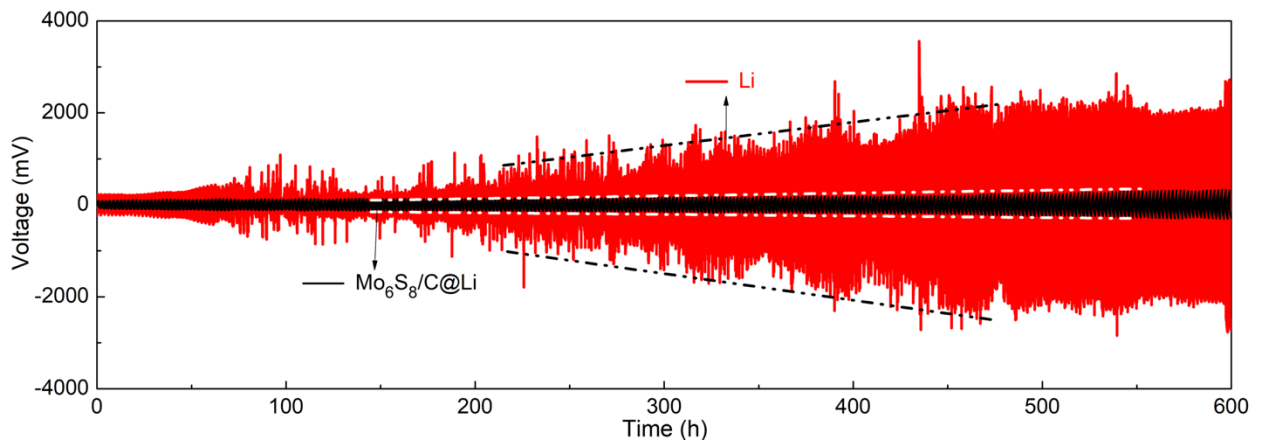


Figure S 7: The $\text{Mo}_6\text{S}_8/\text{C}$ coated Li metal anode show substantially better cyclic stability compared with pristine Li anodes under symmetric cell configuration (testing at 1.0 mA/cm^2 and 1.0 mAh/cm^2 per cycle).

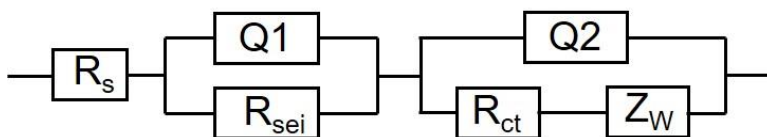


Figure S 8: Equivalent circuit for modeling the electrochemical impedance spectrum acquired from Li metal full cells coupled with NMC-811 cathodes. The parameters R_s , R_{sei} and R_{ct} represent the electrolyte resistance, solid electrolyte interface (SEI) resistance and the charge transfer resistance, respectively; $Q1$ and $Q2$ represent the constant phase elements; Z_w represents the Warburg impedance.

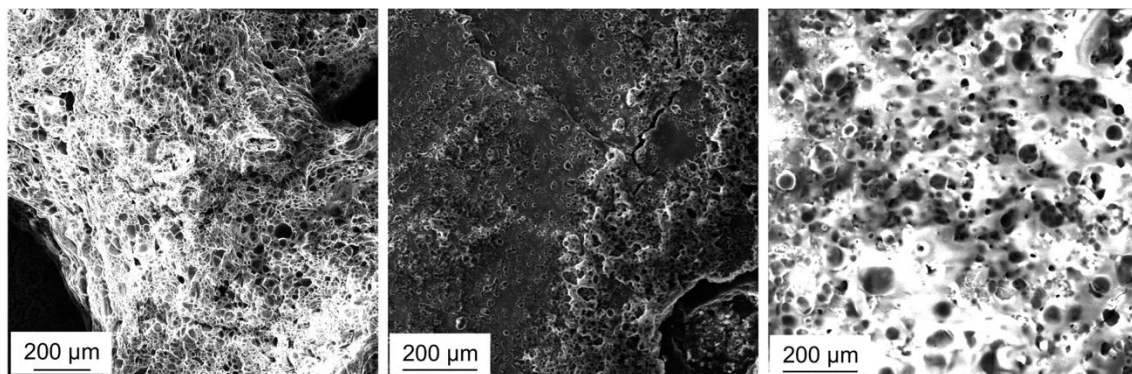


Figure S 9 : Additional post-mortem SEM images acquired from pristine Li metal anode after being cycled for 200 cycles with the NMC-811 cathodes in carbonate electrolyte.

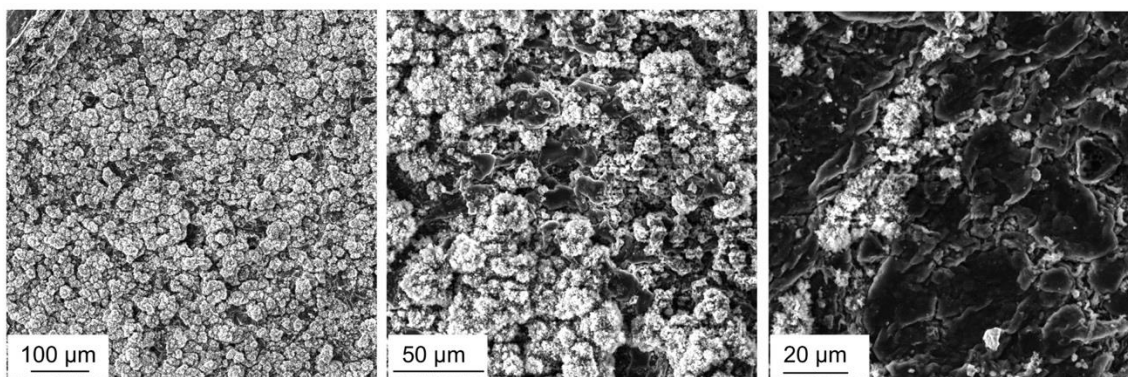


Figure S 6: Additional post-mortem SEM images acquired from hybrid Li metal anode after being cycled for 200 cycles with the NMC-811 cathodes in carbonate electrolyte. The bright agglomerated particles are $\text{Mo}_6\text{S}_8/\text{C}$ composites and the black colored substrate underneath is Li metal.

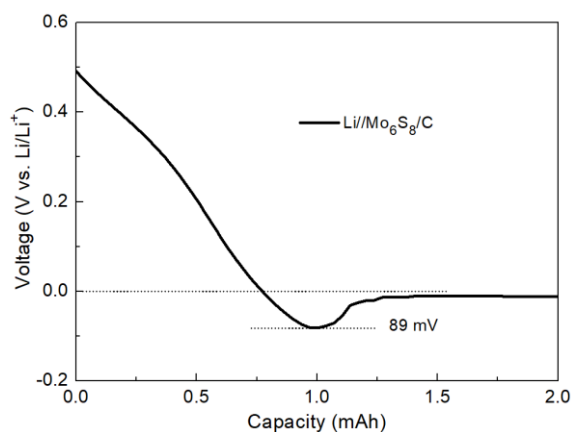


Figure S 11 : Voltage profiles of the initial lithiation process of $\text{Mo}_6\text{S}_8/\text{C}$ electrode, the current density was 2 mA cm^{-2} .

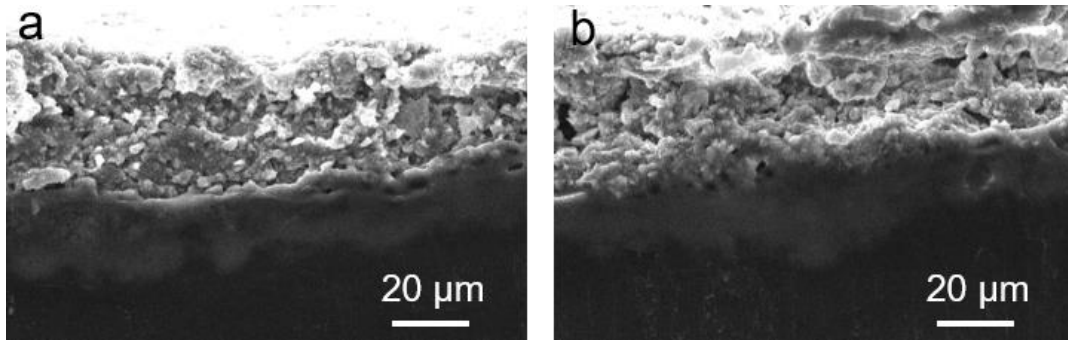


Figure S 7: SEM images of the interphase between Mo₆S₈/C layer and Li metal (a) before and (b) after the 200 cycle test.