Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

In-situ Formation of a Bifunctional Interlayer Enabled by Conversion Reaction to Initiatively Prevent Lithium Dendrite in Garnet Solid Electrolyte

Jiamin Fu,[abc†] *Pengfei Yu,*[a†] *Nian Zhang,**[a] *GuoXi Ren,*[ac] *Shun Zheng,*[ac] *Wencheng Huang,*[ac] *Xinghui Long,*[ac] *Hong Li,*[de] and *Xiaosong Liu**[abe]

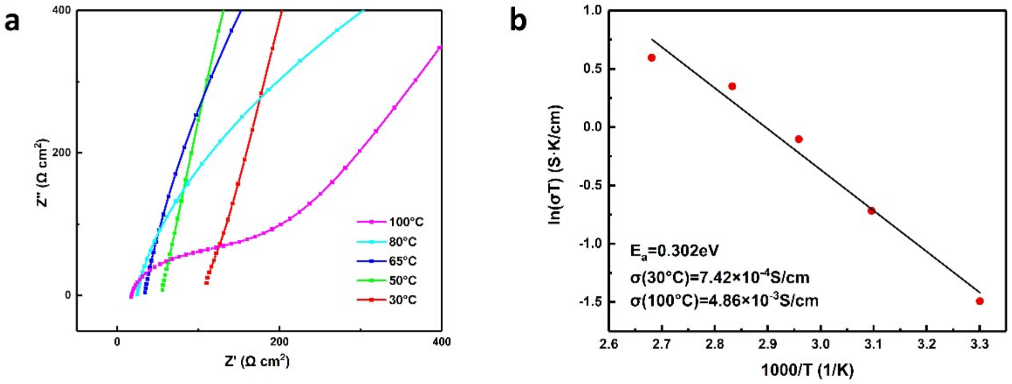

Figure S 1 (a) The electrochemical impedance plot and (b) the temperature dependence of Li-ion conductivities of the LLZO pellet. The activation energy was determined to be 0.302 eV. The ionic conductivity of the LLZO pellet was measured to be 7.42 x 10^{-4} S/cm and 4.86 x 10^{-3} S/cm at 30°C and 100°C, respectively.

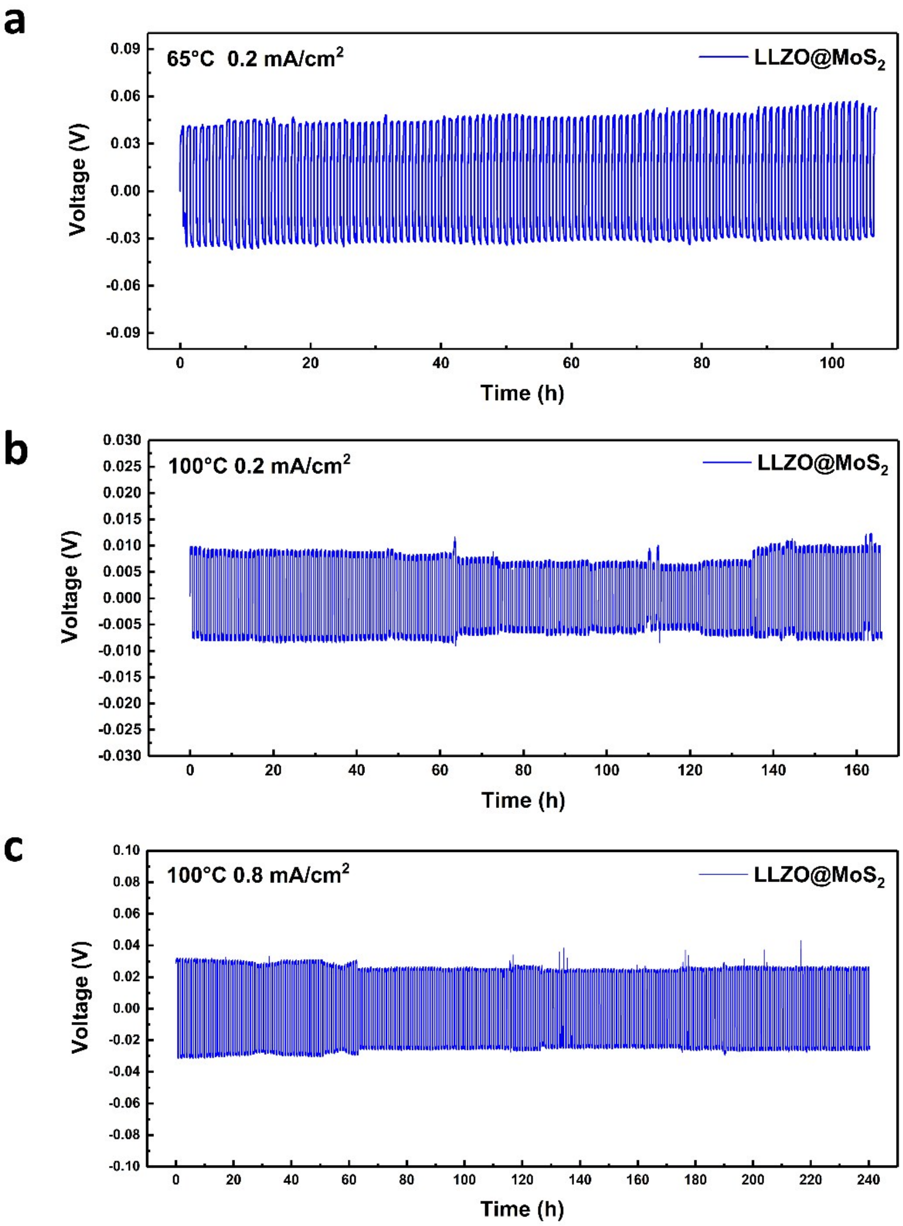

Figure S 2 Charge and discharge voltage profiles of a Li/LLZO@MoS_2/Li at 0.2 mA cm^{-2} at 65 °C (a) and at 100 °C (b). (c) Charge and discharge voltage profiles of a Li/LLZO@MoS_2/Li at 0.8 mA cm^{-2} at 100 °C. The voltage fluctuation in the figure is caused by the temperature change of oven.

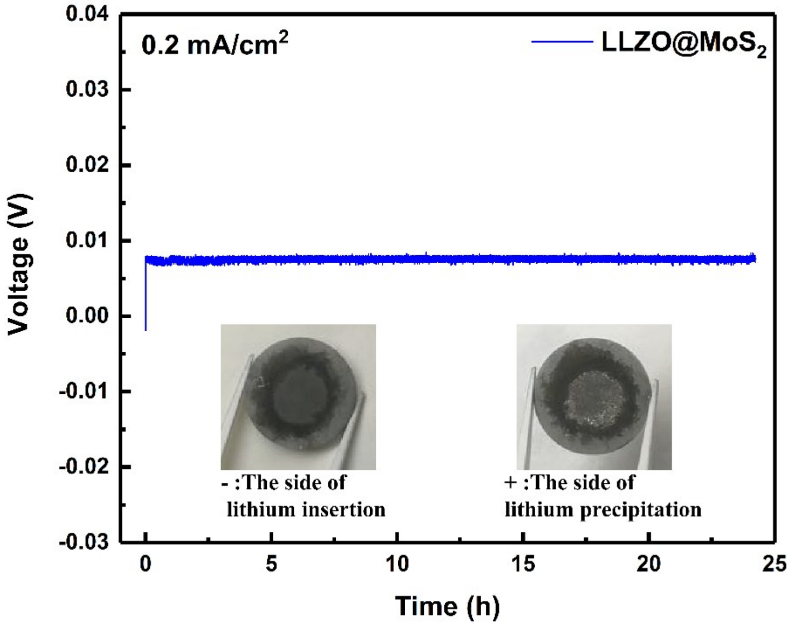

Figure S 3 Constant dc experiments of Li/LLZO@MoS$_2$/Li at current density of 0.2 mA/cm^2 at 100 °C. This test of Li/LLZO@MoS$_2$/Li cell with 0.2 mA/cm^2 maintain more than 24 hours, refer to calculated capacity of 4.8 mA h/cm^2. The inset pictures reveal that the obvious lithium precipitation could be observed on one side of the pellet (+), and that the other side(-) is free of lithium precipitation, indicating that Li-ions were transmitted from one side to the other.

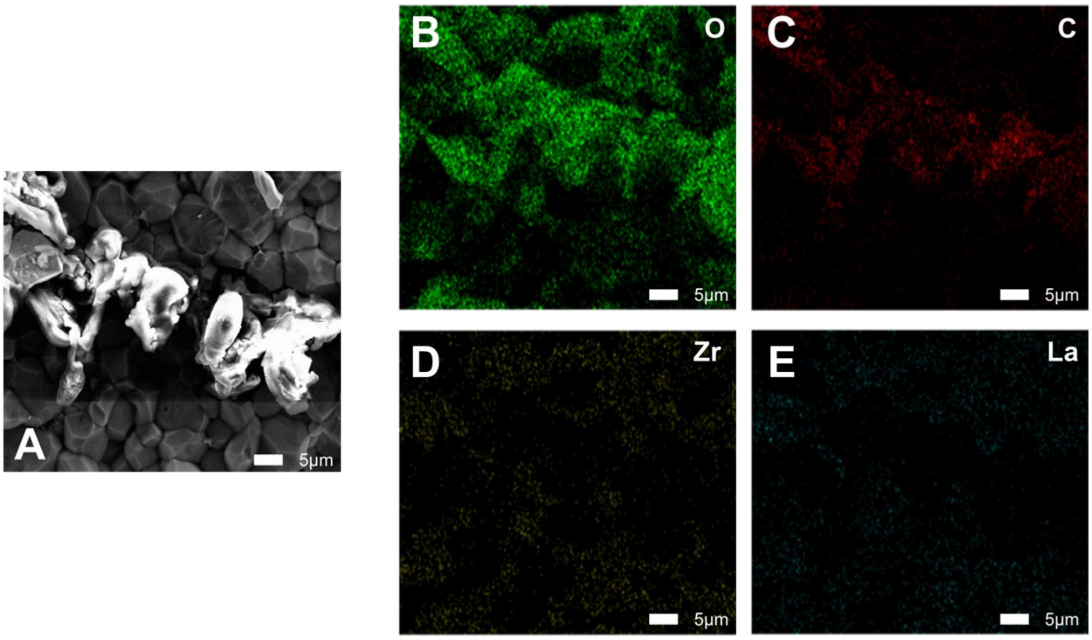

Figure S 4 (A) The cross-section SEM image and (B-E) elemental mappings of C, O, Zr, and La of shorted LLZO pellet. An obvious C, O aggregation could be observed in the distinct line, which was reported to be the product of oxidized Li dendrites reacted with air.

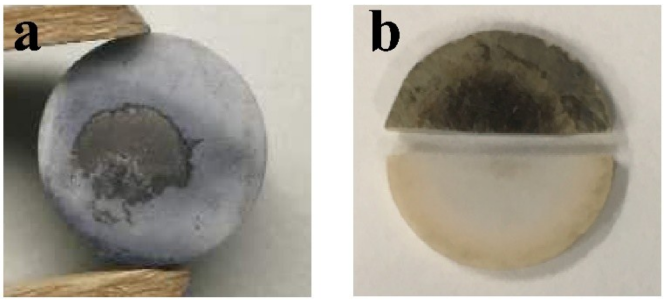

Figure S 5 (a) The optical image of LLZO@MoS_2 pellet that direct contact with lithium at 100 °C for 2 hours. The color change indicates MoS_2 can react with lithium at 100 °C. (b) The optical image of polarized LLZO@MoS_2 pellet. A fresh surface can be reappeared completely after washing the polarized LLZO@MoS_2 pellet with the mixture of water and alcohol.

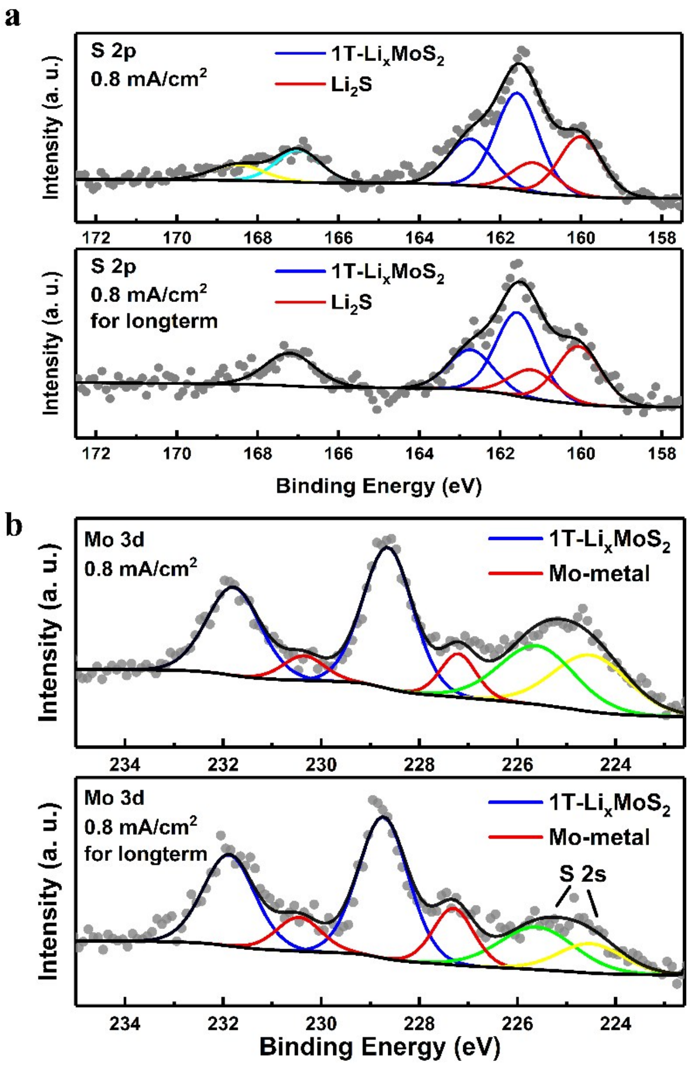

Figure S 6 (a) S-2p XPS spectra of the short-term-cycled sample (cycled at 0.8 mA/cm^2 for 15 hours) and the long-term-cycled sample (cycled at 0.8 mA/cm^2 for more than 240 hours). (b) Mo-3d XPS spectra of the two samples. After the longer operation, the ratio of the intercalated Li_xMoS_2 compound at the Li/MoS_2 does not change greatly. It confirms that the Li/LLZO@MoS_2/Li could work stably at low current density.

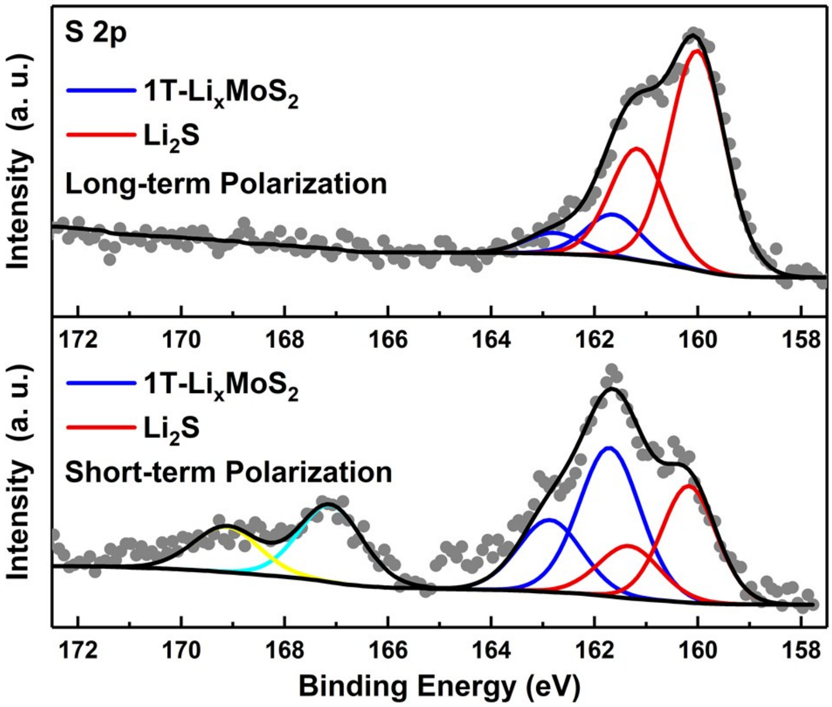

Figure S 7 S-2p XPS spectra of the short-term-polarized sample, which was stopped immediately after the polarization, and long-term-polarized sample that was held at the polarized state for more than half an hour. In our hypothesis, if the current is set too large to be maintained by Li^+ transport, the overpotential will increase continuously, making the conversion reaction occur, and the interlayer becomes more thicker continuously. As shown in the results, the intensity ratio of Li_2S increases dramatically after long-term polarization compared with that of short-term polarized sample. It confirms that the interlayer cannot maintain stable at polarized state and would continuously thicken.

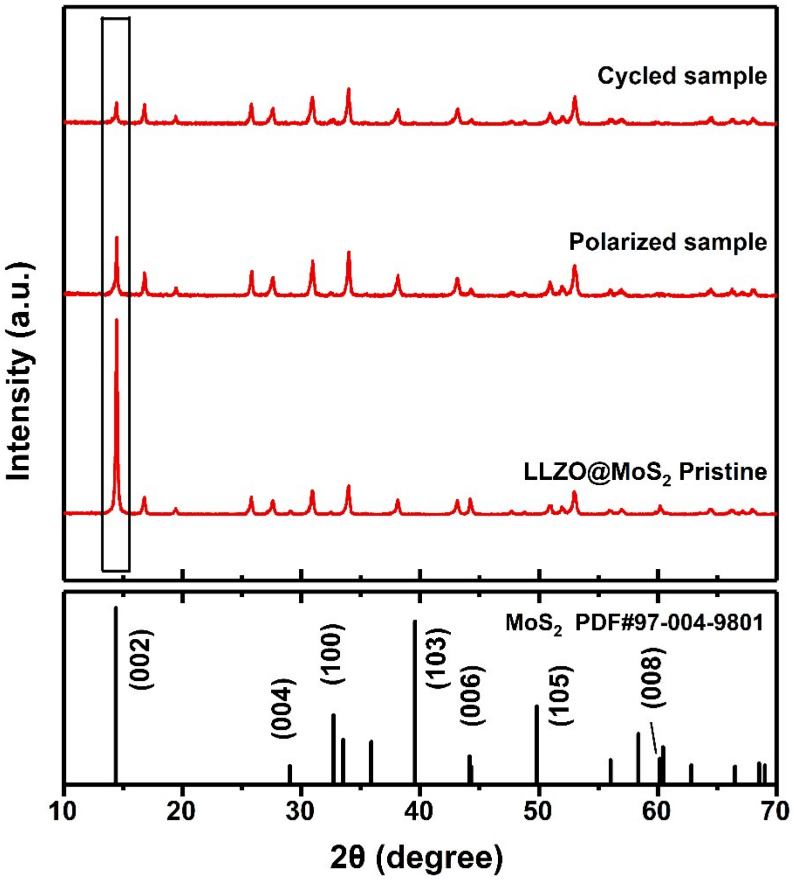

Figure S 8 XRD patterns of different stages (pristine, cycled at 0.2 for 15 hours, short-term polarization) of symmetric Li/ LLZO@MoS_2/Li cells. All the peaks in different samples can be attributed to garnet LLZO and MoS_2, indicating that there are no further reactions in bulk materials. The intensity of MoS_2 (002) diffraction peak of polarized sample dramatically decreased when compared with pristine sample. This peak further decreases in the sample that cycles for 15 hours at 0.2 mA/cm^2. We believe the main reason for the phenomenon is that lithium ions insert into the bulk MoS_2, which damages the periodic symmetry of the crystal structure of MoS_2 in the c-direction.

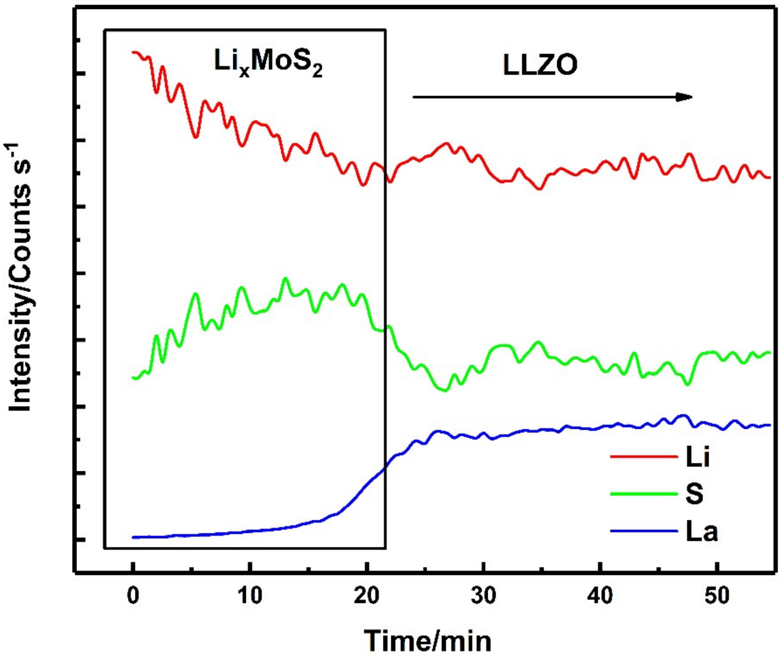

Figure S 9 The intensity of element Li, S, La depth profile in the direction perpendicular to the LLZO pellet. The cell was cycled at 0.2 mA/cm^2 for 15 hours. The main component sputtered by Ar-ions may be Li$_x$MoS$_2$ (represented by Li and S) in initial 20 minutes and then be LLZO (represented by La) after 20 minutes. The transition between the MoS$_2$ layer and LLZO pellet is not sharp, owing to a certain roughness of the original surface of the LLZO pellet. From the Li/MoS$_2$ interface to the MoS$_2$/garnet interface, the intensity of lithium is gradually reduced. This result evidences that the Li/MoS$_2$ interface are more critical for the suppression of mental dendrites because the dendrites preferentially form at areas with high lithium ion concentration.

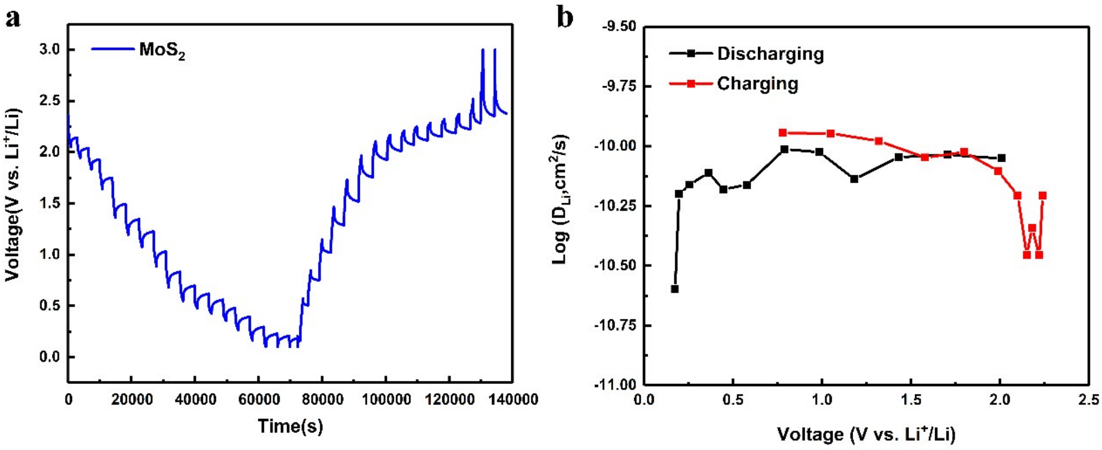

Figure S 10 (a) Galvanostatic intermittent titration technique (GITT) profiles of MoS_2 electrodes cycled in 1.0 M $LiPF_6$ in EC/DMC. (b) Calculated Li^+ diffusion coefficient at discharging and charging process.

The ionic conductivity and the electronic conductivity are valuable for evaluating the performance of coating layers, but it is difficult to directly determine the conductivity of coating layers on the LLZO pellet since Li metal would inevitably adhere on the surface to affect the measurement. Therefore, Li-MoS_2 batteries were prepared to simulate the coating layers. The working electrodes were fabricated by mixing the active material MoS_2, carbon black, and polyvinylidene fluorides with a weight ratio of 8:1:1, respectively. To determine the kinetics of Li^+ diffusion, we employed a galvanostatic intermittent titration technique (GITT) to analyze the Li intercalation of MoS_2 electrode and to give some clues about the ionic conductivity. The standard electrode was discharged and charged at 200 mA/g for 15 min, and then relaxed under open circuit for 1 h. According to the GITT profiles (Figure S10 (a)), the apparent chemical diffusion coefficient (D_{Li}) of Li^+ at a function of voltage was calculated, where the D_{Li} is within 10^{-10}-10^{-11} cm^2/s, corresponding with the work of Zhiqiang Zhu et al.[1] and Ting-Tian Shan et al.[2] Therefore, according to the Nernst-Einstein equation and the calculated D_{Li}, the ionic conductivity of MoS_2 (σ) could be estimated about 10^{-5} S/cm in average (25 °C).

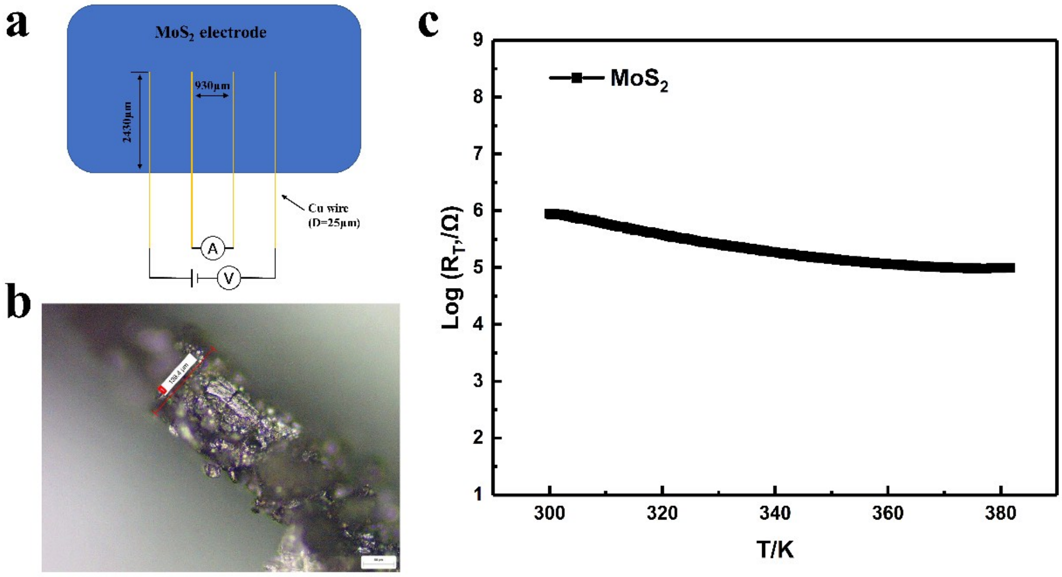

Figure S 11 (a) the test model of MoS_2 electrode using Four-terminal Kelvin Sensing. (b) the cross-section of discharged MoS_2 electrode (Cu foil has been peeled). (c) the profile of total resistance versa temperature.

To measure the electronic conductivity, carbon-black-free MoS_2-Li batteries (the electrode slurry was prepared by mixing MoS_2, carbon black, and polyvinylidene fluorides with a weight ratio of 9:0:1) were discharge to 0.1 V at 100 mA/g. When the discharge was completed, the cell was detached; the electrode was separated from the cell and washed with dimethyl carbonate (DMC) to clean the residual electrolyte. Then Four-terminal Kelvin Sensing was introduced to determine the electrical impedance of the electrode. As the test model shown in the Figure S11 (a), 4 Cu wires was stick to the electrode. The temperature-resistance curve (Figure S11 (c)) was measured in this model with Physical Property Measurement System (PPMS). The resistance is around 10^5-10^6 Ω and decreases as the temperature improves. Therefore, the calculated electronic conductivity is about 2.25×10^{-5} S/cm at 25 °C, which is much lower than other coating layers—Al (3.5×10^5 S/cm), Au (4.6×10^5 S/cm), and graphite (250 S/cm).

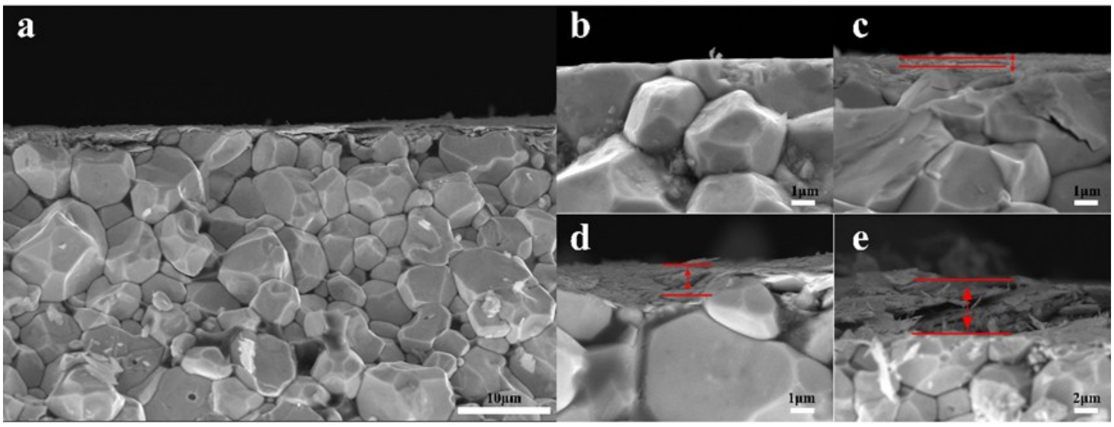

Figure S 12 The SEM cross-section images of samples with or without coating layer. (a) LLZO@MoS_2 with three repetitions at low magnification (×2000). (b) bare LLZO pellet. (c) the LLZO@MoS_2 sample with one repetition. (d) the LLZO@MoS_2 sample with three repetitions. (e) the LLZO@MoS_2 sample with ten repetitions.

LLZO@MoS_2 samples with different thicknesses were prepared by repeating the coating process one time, three times, and ten times on three identical bare LLZO pellets. As shown in the SEM images of the cross section (Figure S12 (a)), MoS_2 sheets are filled in the pits on the LLZO surface, and the surface of coated LLZO is relatively smooth on the micron scale. From the Figure S12 (b) to Figure S12 (e), it is obvious that the more times of coating process are performed, the thicker of MoS_2 layer is coated on the LLZO surface. When the coating process is only conducted once or repeated three times, the thickness is controlled within ~500 nm (Figure S12 (c)) or ~1.5 μm (Figure S12 (d)), respectively. When we repeated the coating process for 10 times, the thickness increases to 6-8 μm as Figure S12 (e). However, the coating layer of ~6-8 μm becomes non-uniform compared to the thinner ones.

References:

1. Z. Zhu, Y. Tang, Z. Lv, J. Wei, Y. Zhang, R. Wang, W. Zhang, H. Xia, M. Ge and X. Chen, *Angew Chem Int Ed Engl*, 2018, **57**, 3656-3660.
2. T. T. Shan, S. Xin, Y. You, H. P. Cong, S. H. Yu and A. Manthiram, *Angew Chem Int Ed Engl*, 2016, **55**, 12783-12788.