Supporting Information

Amidinothiourea as a new deposition-regulating additive for

dendrite-free lithium metal anode

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1. Experimental section.

1.1 Materials.

The lithium foil (thickness of 1 mm) was purchased from China Energy Lithium Co., Ltd. Celgard 2325 separator was purchased from Canrd New Energy Technology Co., Ltd. Amidinothiourea (ATU) was ordered from Aladdin Reagent (Shanghai) Co., Ltd. The base electrolyte (1 M LiTFSI in 1:1 v/v DOL/DME with 1 wt% LiNO₃) was purchased from DodoChem. The with ATU additive electrolyte (0.02 M_{\screwn} 0.05 M and 0.1 M) were prepared via adding stoichiometric ratio of ATU into base electrolyte in a glovebox. The LiFePO₄ (LFP) was purchased from Kejing (Shenzhen) Co., Ltd. LFP electrodes were prepared by mixing LFP, acetylene black, PVDF (dissolved in NMP) at a mass ratio of 8:1:1, coated on Al foil and eventually dried in a vacuum oven at 110 °C for 12 h. The LFP laminate was cut into a disc (diameter 12 mm) with an area mass loading of active material ~2mg cm⁻².

1.2 Material characterization

The surface morphology of materials was examined by scanning electronic microscopy (SEM, Hitachi S-4800), surface compositions were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha spectrometer). The electrode used for characterization was disassembled in the Ar-filled glove box and washed three times with DME solvent, and then followed by drying until the solvent evaporated completely in a vacuum environment.

1.3 Electrochemical measurement

The 2025 coin cells were assembled in an Ar-filled glovebox (both O_2 and H_2O content below 0.1 ppm) to measure the electrochemical performances. Celgard 2325, with/without ATU additive electrolyte was used as the separator and the electrolyte, respectively. The amount of electrolyte for each coin cell was 60 µL. Galvanostatic charge-discharge and rate capability tests were conducted on LAND battery testing system. Cyclic voltammetry (CV) and electrochemical impedance (EIS) measurements were carried out on the electrochemical workstation (CHI 660E, China). The scanning rate of cyclic voltammetry was 10 mV s⁻¹ and the voltage range from -0.5 to 3 V. The frequency range of EIS was 0.01 Hz-100 kHz. The Tafel plots of Li symmetric cells with or without ATU were tested at a scan rate of 1 mV s⁻¹ from -0.25 to 0.25 V. The Li|LFP full cells were tested galvanostatically within a voltage range of 2.5-4.0 V.

1.4 Theoretical calculation

The calculation was carried out in VASP by using density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchanged-correlation functional. For geometric optimization, the cutoff energy of 500 eV was used to ensure the accuracy of the calculation. The Monkhorst-Pack lattice of $4 \times 4 \times 1$ was used to calculate the progressive surfaces of all models. The convergence setting of structural optimization was 0.1 eV nm⁻¹, and the convergence standard of energy was 10^{-5} eV. The absorption energy of ATU additive on Li metal surface was calculated with the following equations:

$\Delta E = E_{ATU@Li} - E_{Li} - E_{ATU}$

Among that, $E_{ATU@Li}$ represented the total energy of ATU additive absorbed on Li metal surface, E_{Li} stood for the energy of Li metal slab model, while E_{ATU} meant the energy of single ATU molecular. The calculation of DME absorption energy on the Li metal surface was the same as above.



Fig. S1. Cycling stability of Li|Li symmetrical cells with different concentration of ATU additive electrolyte at a current density of 0.5 mA cm^{-2} with a capacity of 1 mAh cm⁻².

The impacts of various ATU additive concentration on the long-term stability of lithium electrodes by assembling symmetrical Li|Li cells have been investigated. The cycling performances of Li anode in base electrolyte with (0 M, 0.02 M, 0.05 M and 0.1 M) ATU additive under the condition at a current density of 0.5 mA cm⁻² with a Li plating capacity of 1 mAh cm⁻² are shown in **Fig. S1**. Compared with the base electrolyte, the cycling performance of the Li|Li symmetric cells with ATU electrolyte additives can be significantly improved. The cell with 0.02 M ATU additive can stably cycle 1600 h, much longer than with the base electrolyte (800 h). When 0.05 M ATU additive is added, the cycle life of Li|Li symmetric cells prolonged to 3500 h under the same condition. However, when the concentration of ATU additive is increased to 0.1 M, the overpotential of the cell begins to improve only after 1700 h. The content of ATU additive significantly affects the performance of the lithium metal anodes and the Li|Li symmetrical cells can show the most stable cycling performance in the electrolyte with 0.05 M ATU.



Fig. S2. Cycling stability of Li|Li symmetrical cells with Base/0.05 M ATU additive electrolyte at various current densities with a capacity of 1 mAh cm⁻².

All in all, compared with Base electrolyte, the 0.05 M ATU additive can remarkably enhance cycle stability and decrease overpotentials (**Fig. S2**). The cycle life at current density of 1, 2, 5, 8 mA cm⁻² with a capacity of 1 mAh cm⁻² of 0.05 M ATU additive electrolyte is 4000, 2500, 2000, 300 h, whereas, the cycle life of Base electrolyte is only 600, 1000, 320, 43 h. For example, at a current density of 5 mA cm⁻², the overpotential of the Base electrolyte gradually increased after 100 h, which could be result from the instability of the generated SEI film. In comparison, the electrolyte with 0.05 M ATU achieved a stable Li plating/stripping behavior over 2000 h with a low overpotential of 100 mV, indicating that the electrolyte with ATU additive can effectively improve the long cycle stability of lithium metal anodes. All of these results suggest that the incorporation of ATU additive can lower the overpotential of symmetrical cell, leading to a stable Li/electrolyte interface during long cycling life.



Fig. S3. EIS of Li|Li symmetric cells at different cycles: a, b) Base, 0.05 M ATU electrolyte.



Fig. S4. Real-time optical images of Li deposition in the base electrolyte (a) and the electrolyte with 0.05 M ATU (b) at a current density of 10 mA cm^{-2} .



Fig. S5. SEM images of Li| Li symmetrical cells after 20 cycles at a current density of 1 mA cm⁻² using a, b) Base electrolyte, 0.05 M ATU electrolyte.



Fig. S6. SEM images of Li deposition after 150 cycles in symmetric cells with (a, c) and without (b, d) ATU



Fig. S7. a) Adsorption energy of ATU molecular on Li metal surface; b) Adsorption energy of DME molecular on Li metal surface.



Fig. S8. SEM images of Li deposited on Cu foil at a current density of 0.5 mA cm⁻² with a capacity of 5 mA h cm⁻²: a, b) Base electrolyte, c, d) 0.05 M ATU additive electrolyte.

Author Contributions

Y. Lei, L. Huang, C.-T. Wang and S.-G. Sun conceived the concept and supervised the project. Y. Lei, Y.-X. Xie, Y.-X. Huang, X.-H. Wu, and Q. Wang performed materials synthesis and characterization and data analysis. Y.-X. Xie, Y.-X. Huang, and X.-H. Wu, P. Dai performed theoretical calculations. Y. Lei, Y.-X. Xie, Y.-X. Huang, Z.-G Li, X.-H. Wu, and carried out battery preparation and electrochemical measurements. Y. Lei, Y.-X. Xie, L. Huang, C.-T. Wang, Y.-J. Hua and S.-G. Sun wrote the manuscript. Y. Lei, Y.-X. Xie, Z.-G Li, Y. Qiao, L. Huang, C.-T. Wang, Y.-J. Hua and S.-G. Sun revised the manuscript. All authors contributed to the discussion of the study.