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Supporting Information

Lithiophilic Ag/Li Composite Anodes via a Spontaneous Reaction for Li Nucleation with Reduced Barrier

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S-1: The theoretical production of lithium nitrate is based on the following calculations. Firstly, the concentration of silver nitrate is 50 mmol L^{-1}, silver nitrate is added in an amount of 100 μL. After evaporating solvents, the amount of electrolyte used is 45 μL. C (mmol L^{-1}) is the concentration of lithium nitrate in the electrolyte. The ether-based electrolytes density ρ is ≈1.10 g cm^{-3}, the molar mass of silver nitrate M is 170 g mol^{-1}. According to the conservation of materials:

$$\frac{100\ \mu L}{45\ \mu L} = \frac{C\ \ mmol\ L^{-1}}{50\ mmol\ L^{-1}} \quad \rightarrow C \approx 0.11\ mol\ L^{-1}$$

$$Wt.\%\ of\ LiNO_3 = \frac{C \times M}{1000 \times \rho} = \frac{0.11\ mol\ L^{-1} \times 170\ g\ mol - 1}{1000 \times 1.10\ g\ cm^{-3}} \approx 1.7\%$$

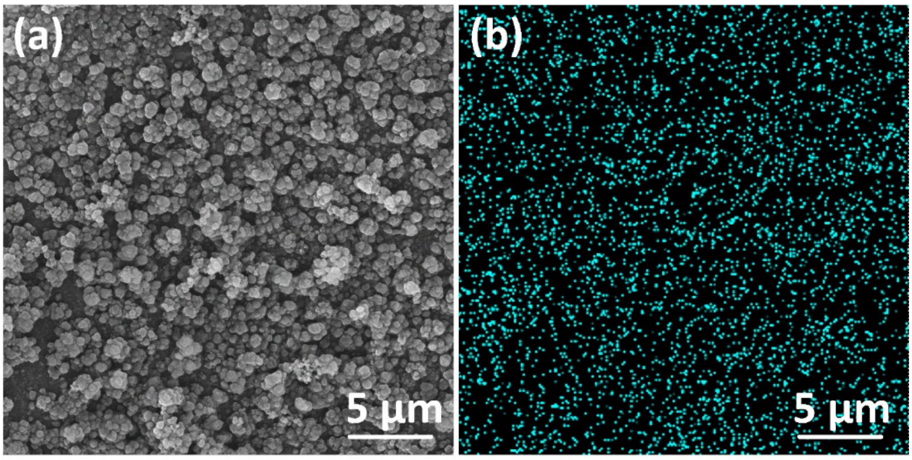

Figure S1. a) SEM image of SSNs before cycling, b) Corresponding EDS mapping of Ag.

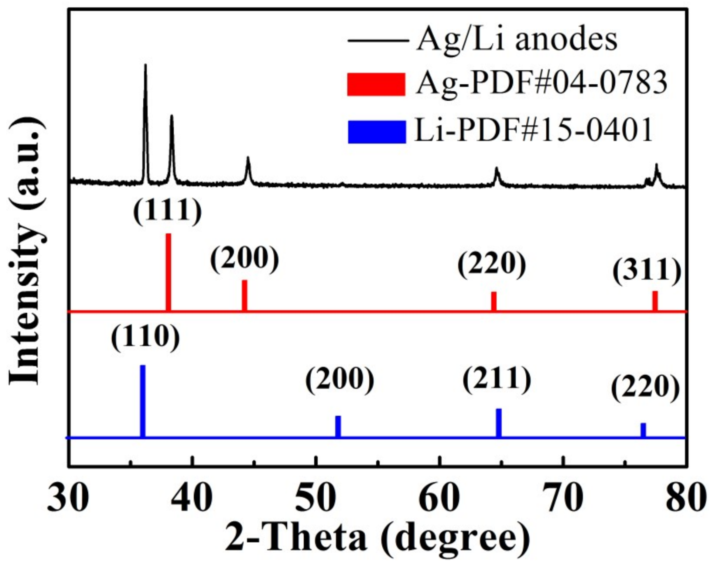

Figure S2. XRD patterns of Ag modified Li anodes before cycling.

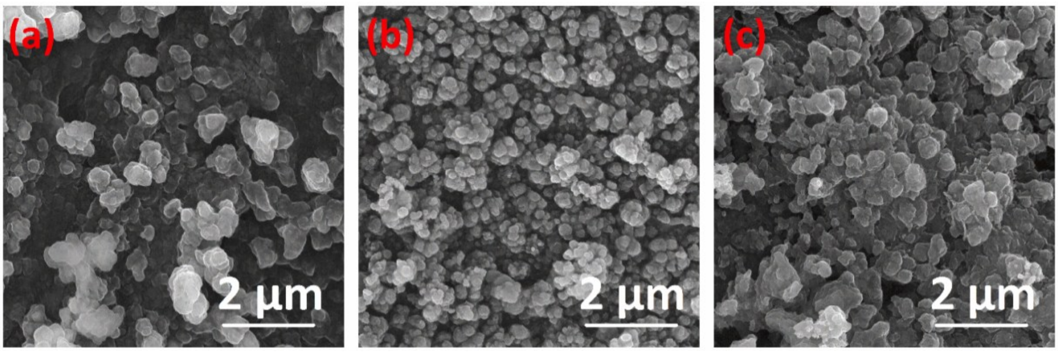

Figure S3. SEM images of SSNs with a) 75 μL, b) 100 μL and c) 125 μL silver nitrate solution.

Figure S3 shows the morphology of SSNs via dropping with silver nitrate solution of 75 μL, 100 μL and 125 μL on Li foils, respectively. When the amount of silver nitrate is 100 μL, SSNs exhibit minimum and homogeneous particle size of ≈350 nm, uniformly distributing on Li foils without apparent agglomeration. Under this experimental conditions, SSNs can provide more electrochemical active sites.

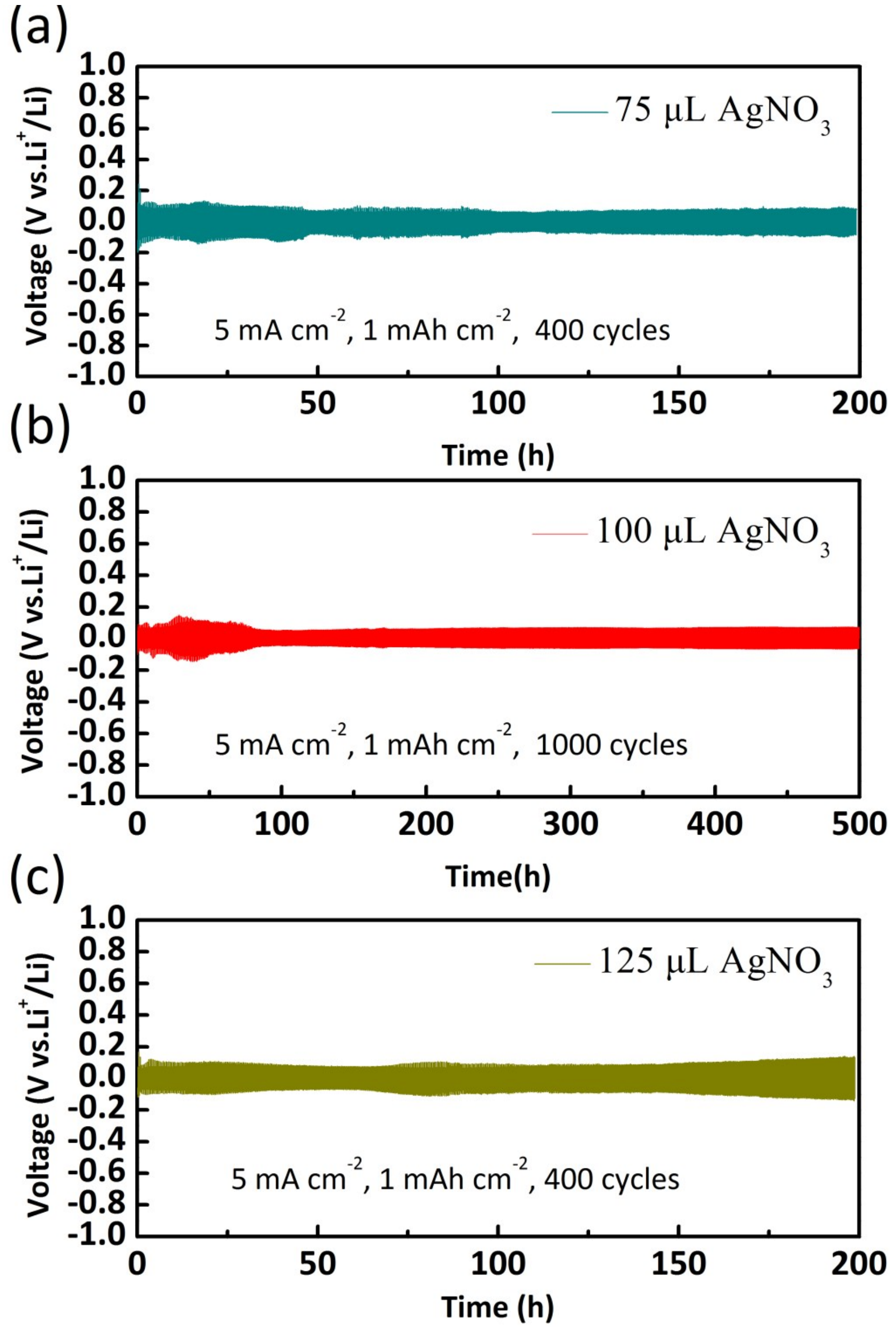

Figure S4. Voltage profiles of Ag/Li symmetric cells dropped with various volumes of silver nitrate solution at 5 mA cm^{-2} with 1 mAh cm^{-2}.

To further determine the effect of SSNs size on Li deposition, symmetric cells with 75 μL,100 μL,125 μL silver nitrate solution were tested at 5 mA cm^{-2} at 1 mAh cm^{-2}. According to the corresponding voltage curves **(Figure S4)**, the symmetric cells with 100 μL silver nitrate solution demonstrate more stable voltage curves, lower overpotential, as well as longer lifespan. Based on the above experiments, we can conclude that the smaller of the Ag particle size (100 μL silver nitrate solution), the better electrochemical performance of Ag/Li anodes for Li deposition. Taking all the assessment of experiments discussed previously, the subsequent experiments are based on silver nitrate content of 100 μL.

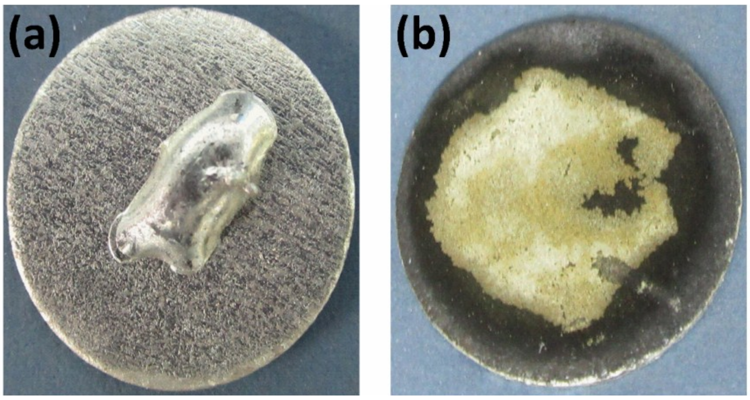

Figure S5. Lithiophilicity experiments of a) bare Li anode and b) Ag/Li anodes with molten Li.

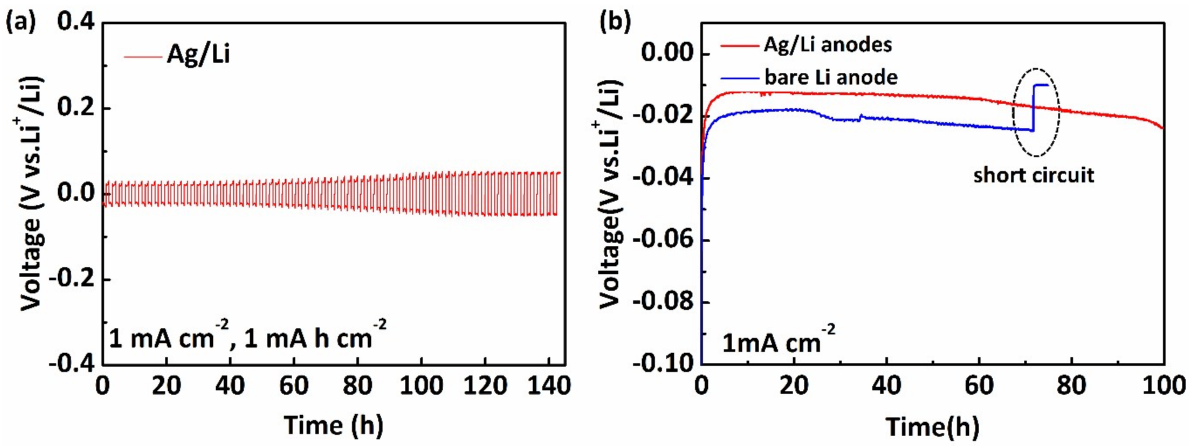

Figure S6. a) Voltage profile of reassembled Ag/Li symmetric cell after 1000 cycles. b) Galvanostatic discharge tests of Ag/Li symmetric cell (red) and bare Li symmetric cell (blue) at 1 mA cm^{-2}.

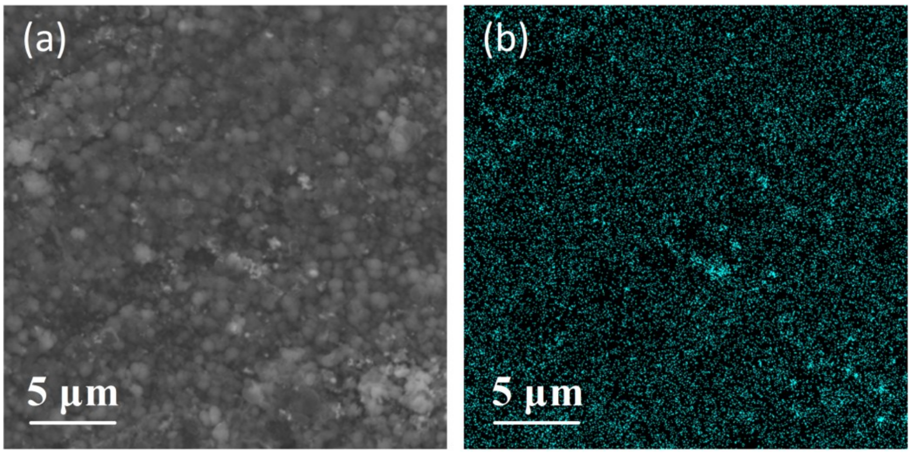

Figure S7. a) SEM image of Ag/Li anodes after 500 cycles (5mA cm^{-2}, completely stripping). b) Corresponding EDS mapping of Ag.

We observed the morphology of cycled Ag/Li anodes (5mA cm^{-2}, completely stripping) to explore the motion and distribution of SSNs. According to the SEM images and EDS mapping (**Figure S7**), the SSNs re-exposed after 500 cycles (stripping), and the distribution of SSNs is still random and uniform. The results indicate that SSNs are extremely stable, which can repeatedly guide Li nucleation and deposition.

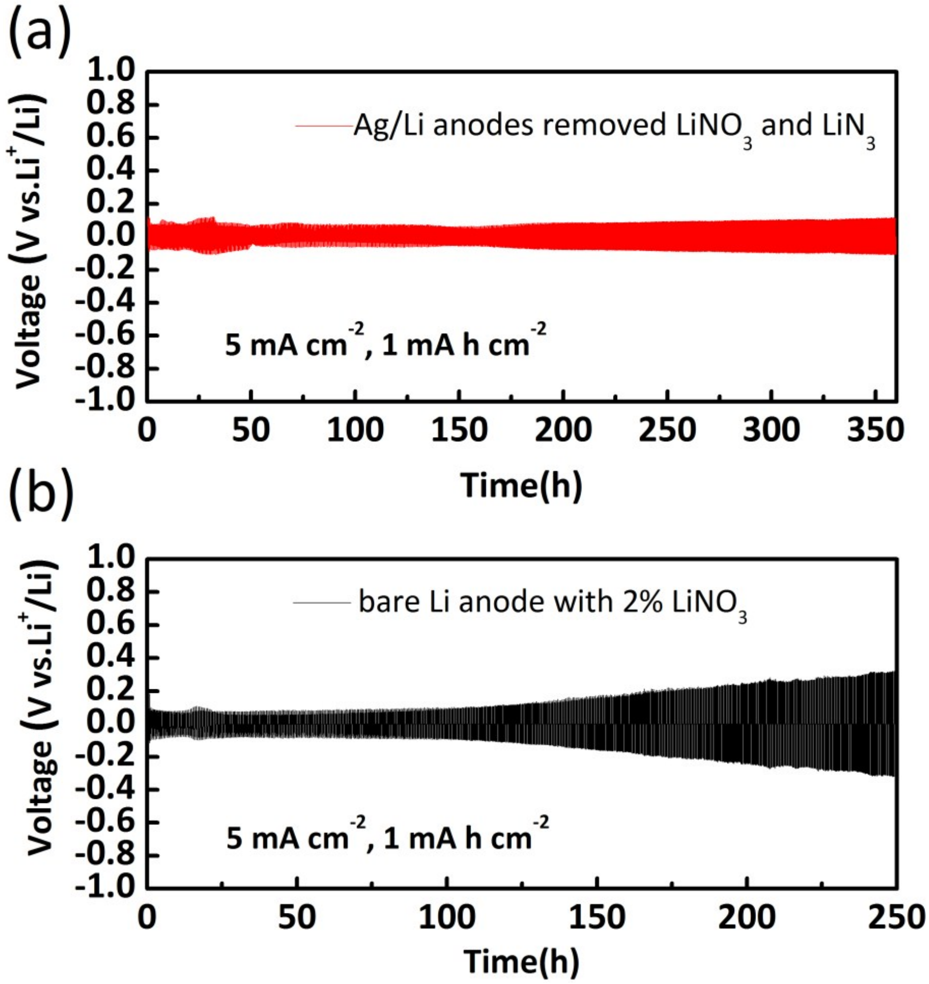

Figure S8. a) Voltage profile of Ag/Li symmetric cells removed the generated $LiNO_3$ and LiN_3. b) Voltage profile of bare Li symmetric cells with 2 % $LiNO_3$.

$LiNO_3$ and LiN_3 are reported to serve as additives to stabilize Li deposition. Since they can inhibit Li dendrites via generate uniform and stable SEI films (mainly Li_3N) [1-3]. To evaluate the role of $LiNO_3$ and LiN_3 on Li deposition, the generated $LiNO_3$ and LiN_3 are carefully washed by the DME/DOL. Then the Ag/Li symmetric coin cells were tested in the same conditions (5 mA cm^{-2}, 1 mA h cm^{-2}). Although the symmetric cells of Ag/Li anodes can cycle for about 800 cycles (**Figure S8a**), a relatively large voltage fluctuation occurs after 355 cycles (160 h). The overpotential is 0.11 V after 800 cycles, which is larger than the group retaining the generated $LiNO_3$ and LiN_3 (**red curve in figure 5b**). The consequence verifies the positive effect of generated $LiNO_3$ and LiN_3 on the repeated Li deposition.

Moreover, bare Li symmetric cells with 2% $LiNO_3$ also were tested to investigate the effect of $LiNO_3$ on Li deposition (**Figure S8b**). This group can stably work about 100h (225 cycles) with stable voltage curve, which is better than the counterpart group without $LiNO_3$ (**blue curve in figure 5b**), indicating the positive effect of $LiNO_3$ when used as an electrolyte additive. Based on the experiments, we can conclude that the generated $LiNO_3$ and LiN_3 have a positive effect on Li deposition. However, the Ag/Li anodes play more important role than the generated $LiNO_3$ and LiN_3 for Li deposition in this experiment.

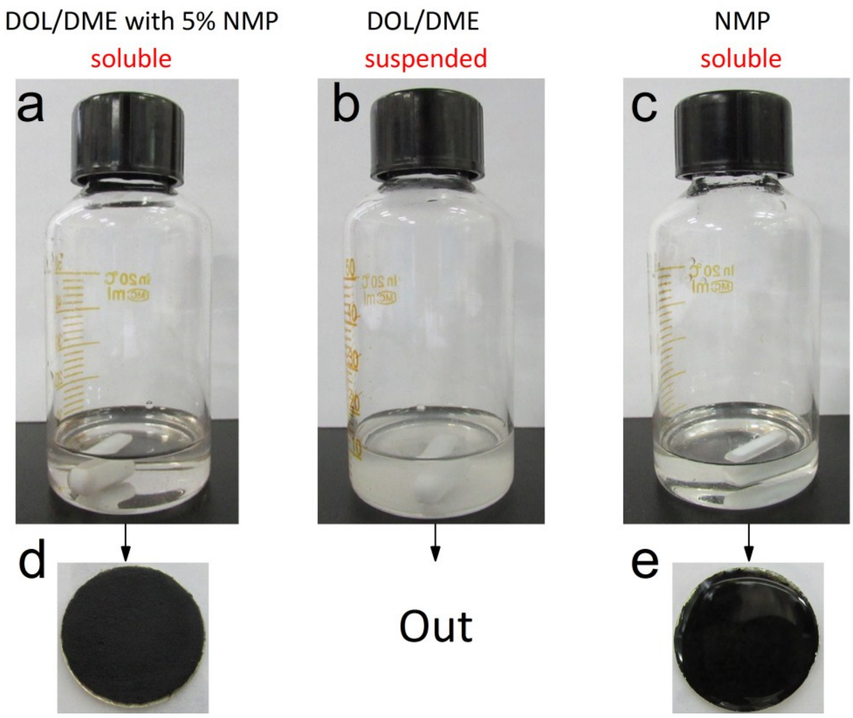

Figure S9. a-c: the camera images of silver nitrate in various solvents. d-e: Li foils with 100 μL of silver nitrate solution (0.05 mol L^{-1}) after 1 hour. The Li foil dripped with DOL/DME With 5% NMP has dried out, but the Li foils with pure NMP are still wet. These images indicate DOL/DME With 5% NMP is most suitable. Since in this solvent system, the silver nitrate can be soluble and rapidly evaporated.

Table S1. The fitted resistance parameters of symmetric cells before cycling, after 1 cycle, and 50 cycles with 1 mA h cm^{-2} at 1 mA cm^{-2}.

Symmetric cells	Ag/Li anodes		Bare Li anode	
Cycle number	R_{SEI} (Ω)	R_{ct} (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
Before cycling	10.66	42.69	0	72.68
1 cycle	4.00	16.69	4.68	24.60
50 cycles	1.13	11.60	1.89	17.15

References

1. W. Li, H. Yao, K. Yan, G. Zheng, Z. Liang, Y. M. Chiang and Y. Cui, Nat Commun, 2015, 6, 7436.
2. C. Yan, Y.-X. Yao, X. Chen, X.-B. Cheng, X.-Q. Zhang, J.-Q. Huang and Q. Zhang, Angewandte Chemie International Edition, 2018, 57, 14055-14059.
3. G. G. Eshetu, X. Judez, C. Li, O. Bondarchuk, L. M. Rodriguez-Martinez, H. Zhang and M. Armand, Angew Chem Int Ed Engl, 2017, 56, 15368-15372.