Supplementary Information

Suppression of Dendritic Lithium Growth by In-situ Formation of a Chemically Stable and Mechanically Strong Solid Electrolyte Interphase

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Calculation of apparent Young`s modulus of SEI

The modified Sneddon model was applied to calculate Young`s modulus of SEI. The relationship between loading force *F* and the indentation depth δ are below：

$$F = \frac{2}{\pi} \frac{E}{1-\upsilon^2} \tan\alpha \, \delta^2 \quad (1)$$

In which E is Young`s modulus of sample. Assuming the SEI is rubber elasticity in elastic region, Poisson raio, υ is set to be 0.5. The half side angle α of cantilever is 18º. The Young`s modulus of *E* can be obtained from the slope of fitting curve within linear region in F-δ^2 plots.

Supplementary Figures

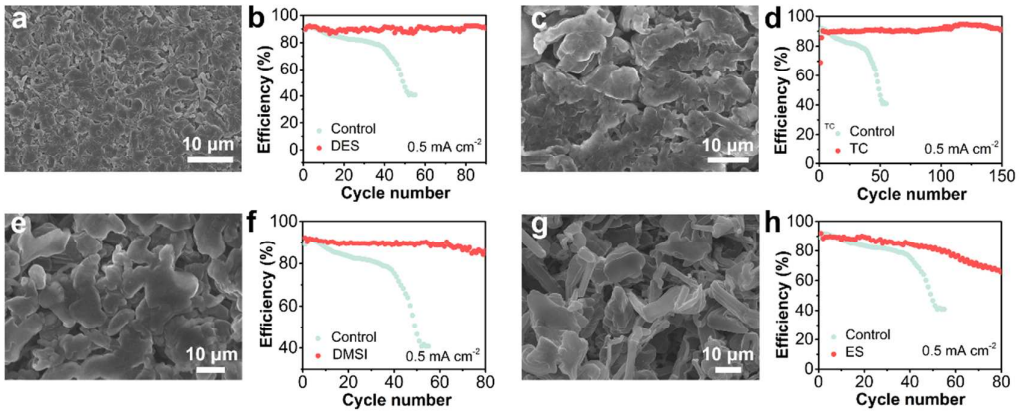

Figure S1. SEM images of Lithium deposition and Coulombic efficiency of various organic sulfate ,sulfite additive in 1 M $LiPF_6$ EC/DMC. a,b) Dimethylsulfate (DES); c,d) Thionyl chloride (TC); e,f) Dimethyl sulfite (DMSI); g,h) Ethylene sulfate (ES). All Coulombic efficiency were tested under 0.5 mA cm^{-2} with a capacity of 1.0 mAh cm^{-2}.

In this work, we had compared the electrochemical behaviors of several sulfonyl-based compounds, including DMS, DES, TC, DMSi and ES. As shown in Figure 5 and S1, it is found that DMS demonstrated best overall performance in terms of Coloumbic efficiency, cycling stability and Li deposition morphology than other additives. This superior performance could be attributed to the highest content of sulfur-oxygen elements in DMS molecule, thus it could introduce more Li_2S/Li_2O species into SEI layer. As a result, SEI with more inorganic species has better mechanical property and ionic conductivity, contributing to build a more stable Li anode.

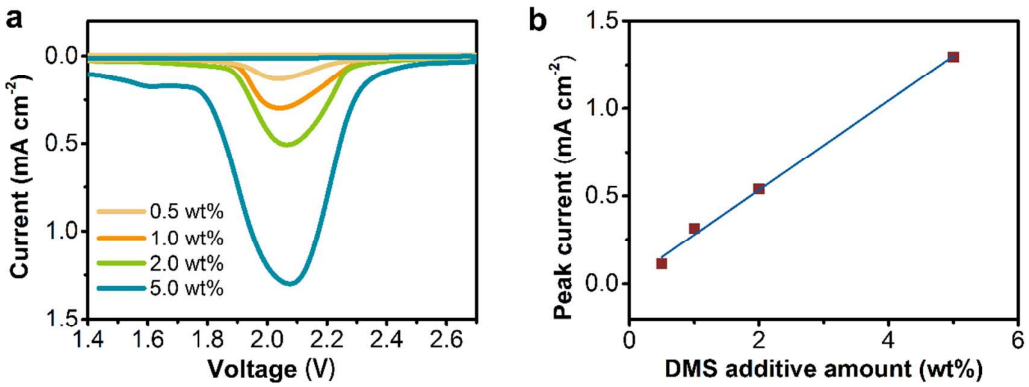

Figure S2. a) Cyclic voltamogram of electrolytes with a series of concentration of DMS in the region of 1.4-2.6 V at scan rate of 0.5 mV s^{-1}; b) Relationship of peak current intensities with added amounts of DMS in the electrolyte.

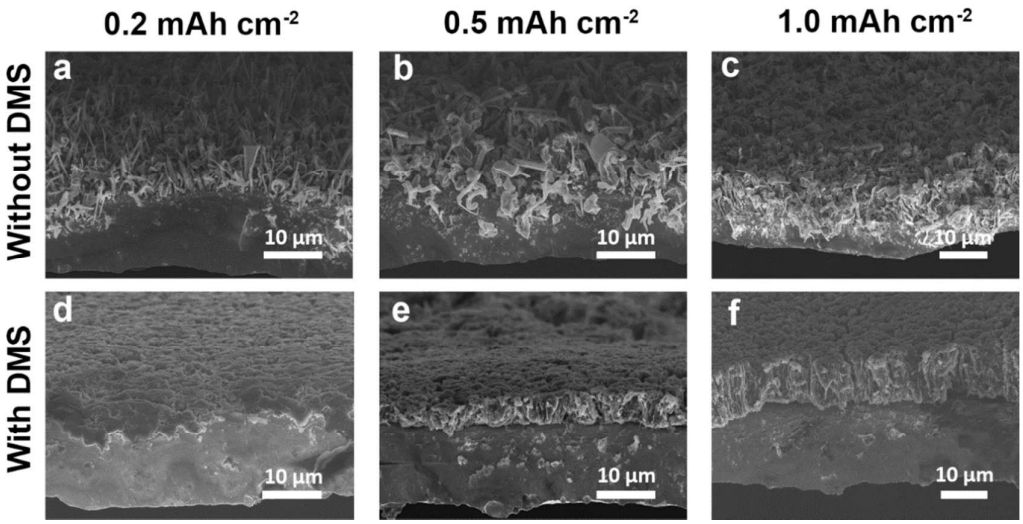

Figure S3. Morphologies characterization of lithium initial deposition on Cu substrate at 0.2 mAh cm^{-2}, 0.5 mAh cm^{-2}, 1.0 mAh cm^{-2}. SEM images of Li deposited in electrolyte (1.0 M $LiPF_6$ EC/DMC) without DMS (a-c) and with 1 wt% DMS (d-f) at a current density of 0.5 mA cm^{-2}.

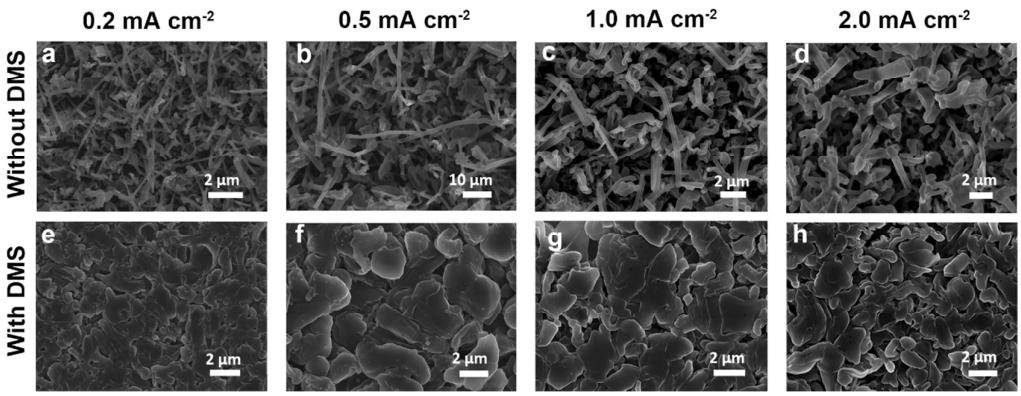

Figure S4. SEM morphologies of Li deposition under a constant current density of a, e) 0.2 mA cm^{-2}, b, f) 0.5 mA cm^{-2}, c, g) 1.0 mA cm^{-2}, d, h) 2.0 mA cm^{-2}.

A serious of SEM images of deposited Li using electrolyte with or without DMS under various current densities ranged from 0.2 mA cm^{-2} to 2.0 mA cm^{-2} were provided in Figure S4. As shown in Figure S4, even in higher current densities of 1.0 mA cm^{-2} and 2.0 mA cm^{-2}, the morphologies of Li deposition using DMS keep compact and nodule-like. In contrast, control samples display dendritic Li with porous structure.

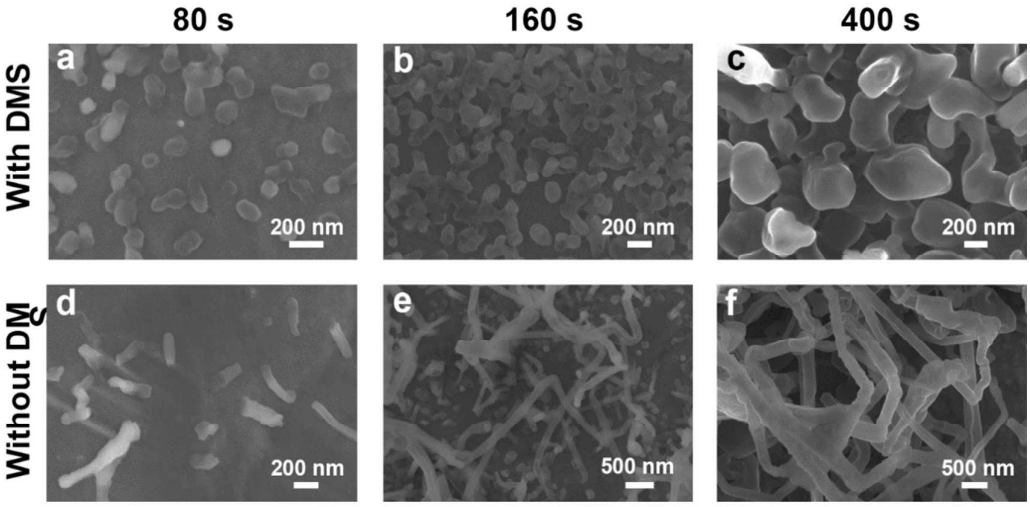

Figure S5. SEM morphologies of Li nucleation process. a-c) With 1 wt% DMS at discharge time of 80 s,160 s,400 s. d-f) Control electrolytes at discharge time of 80 s, 160 s, 400 s. Constant discharge density was 0.5 mA cm^{-2}.

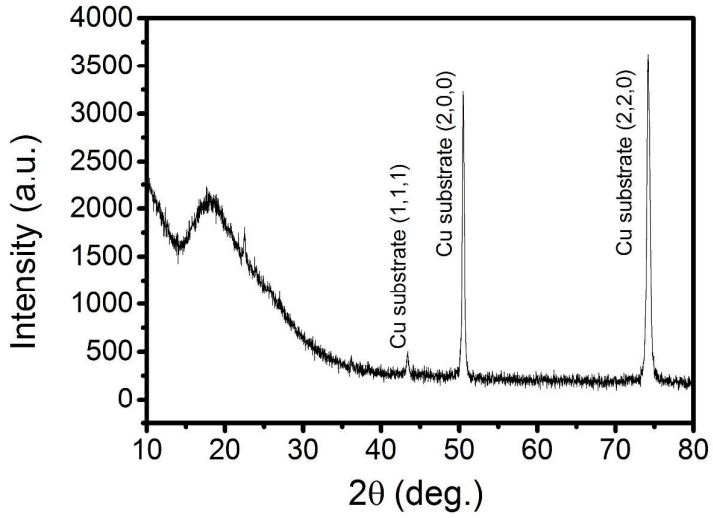

Figure S6. XRD spectra of deposited lithium in 1% wt DMS added electrolyte.

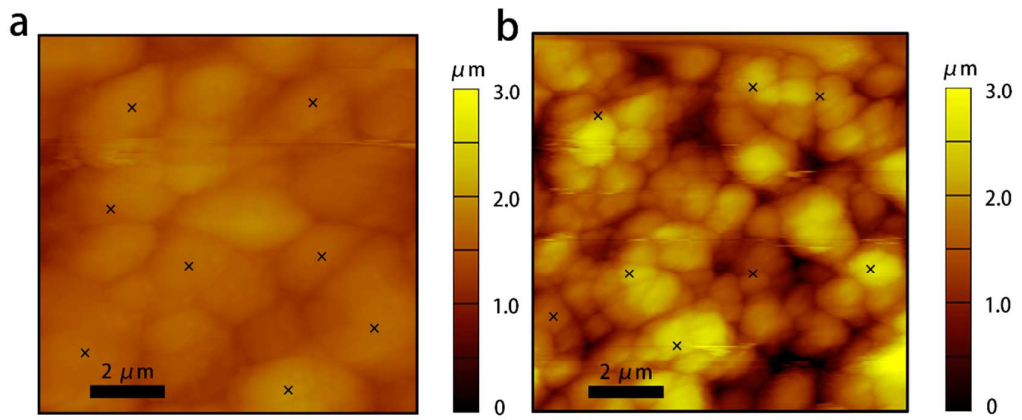

Figure S7. Topographic of Lithium deposition on Cu foil. a) With DMS. b) Control sample. A series single point of young`s modulus were detected at position marked by "X" in above figures. Their value were listed in Table S1.

With DMS	Young`s Modulus / Gpa	Control	Young`s Modulus / Gpa
1	1.89	1	0.31
2	2.11	2	0.45
3	1.78	3	0.41
4	1.99	4	0.09
5	2.02	5	0.56
6	1.67	6	0.23
7	1.75	7	0.46
8	1.94	8	0.28
$\bar{X}$	1.89	$\bar{X}$	0.35

Table S1. The young`s modulus of SEI with or without DMS.

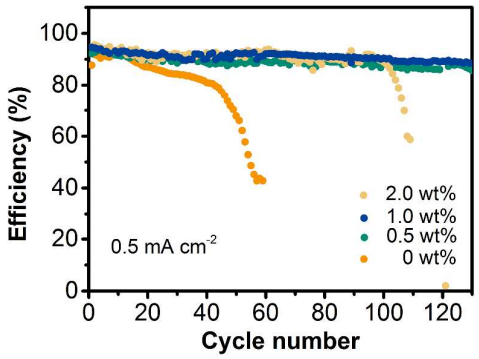

Figure S8. Coulombic efficiency of electrolytes with addition of different amount of DMS (0.5 wt%, 1 wt% and 2 wt%) under a constant current of 0.5 mA cm^{-2} with capacity of 1.0 mAh cm^{-2}.

Li|NCM full cells cycling performance test

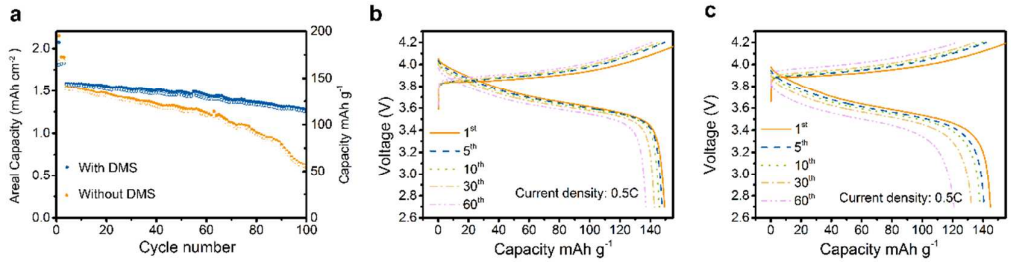

Figure S9. Cycling stability and polarization voltage profiles of Li|NCM cells. a) Capacity vs. cycle number plots. b,c) Polarization voltage profiles with and without DMS in 1.0 M $LiPF_6$ EC/DMC.