Morphological and Chemical Mapping of Columnar Lithium Metal

SUPPLEMENTARY INFORMATION

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All capacities and current densities are areal (per cm^2).

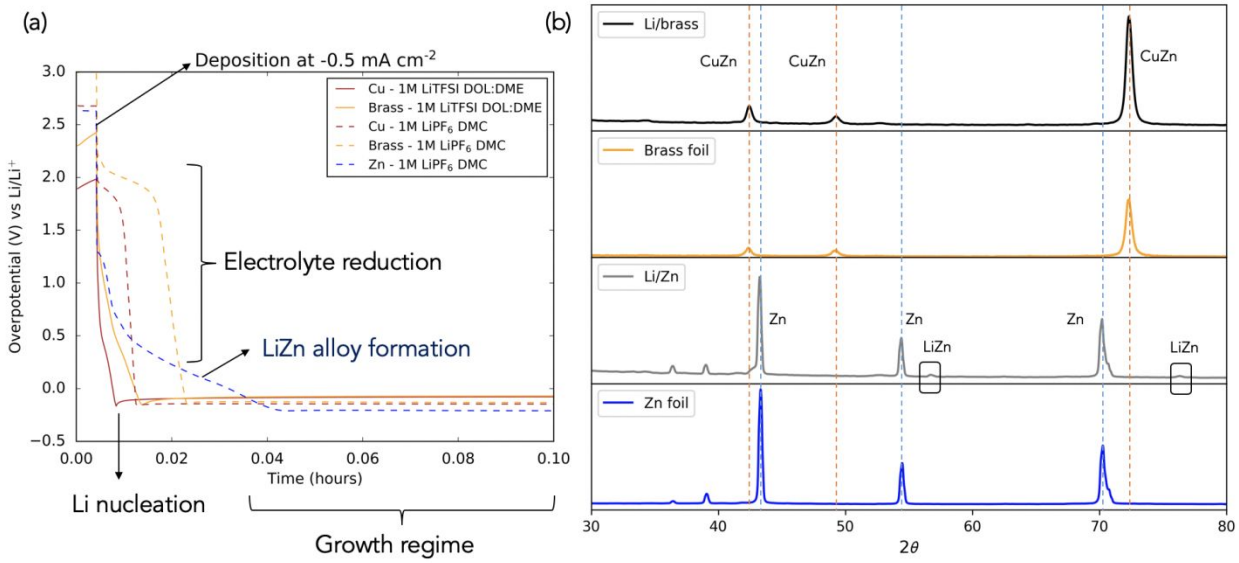


Figure S1. (a) Deposition overpotential (vs Li/Li^+) profiles for Li plating on either Cu and brass, in either 1M LiTFSI DOL:DME and 1M $LiPF_6$ DMC, and Li plating on Zn in 1M $LiPF_6$ DMC. All four profiles for Cu and brass substrates show initial electrolyte reduction and a nucleation peak followed by long-term growth. Deposition on Zn foil shows alloying behavior with no nucleation peak. All depositions were carried out at -0.5 mA cm^{-2}. (b) Corresponding XRD spectra for Li deposited on brass and Zn foil, and brass and zinc foil reference. LiZn peaks can be observed for Li deposited on Zn (see black square), but not for Li deposited on brass.

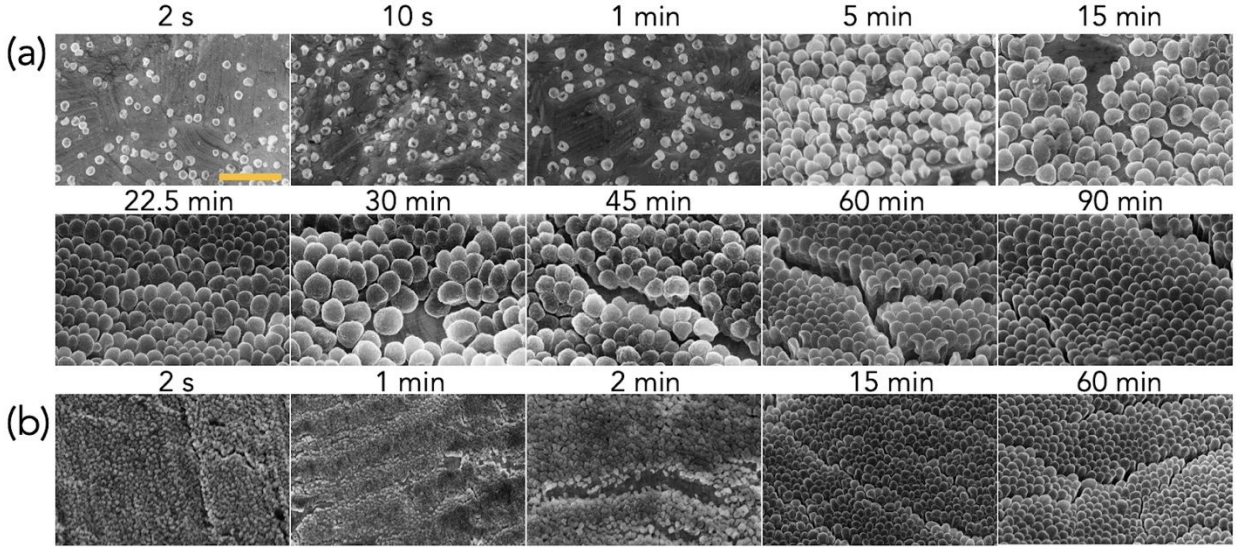


Figure S2. Growth evolution of columnar Li on (a) acid treated stainless steel 321 and (b) acid treated brass ($Cu_{63}Zn_{37}$), at labeled time intervals. Each image was taken after a separate plating carried out at the labeled time interval at 0.5 mA cm^{-2}. All images are at the same magnification,

with the scale bar representing 1 μm. The columnar diameters for brass are noticeably smaller than the diameters for stainless steel. Statistical data on diameters for various substrates are provided in Figure 1. It should also be observed that columnar morphology (growth in vertical direction) starts to appear before the plating becomes completely close-packed. This indicates that the columnar growth may be determined by preferred deposition sites on pre-existing nuclei (an electrochemical effect), rather than a mechanical effect due to SEI formation causing nuclei to impinge upon each other (as suggested by Zhang et al.).

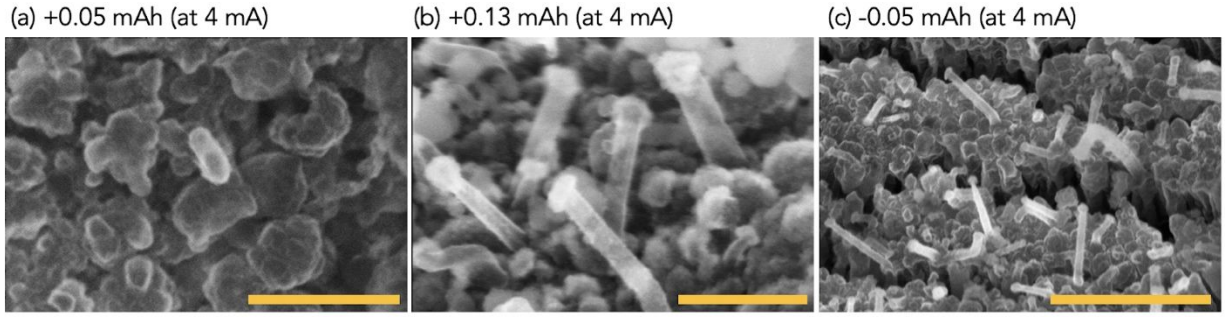


Figure S3. High resolution SEM images of growth protrusions on columnar lithium deposits in 1M $LiPF_6$ DMC, at (a) 4 mA cm^{-2}, 0.050 mAh cm^{-2}; (b) 4 mA cm^{-2}, 0.133 mAh cm^{-2}; and (c) after 0.050 mAh cm^{-2} Li stripped. Scale bars indicate (a) 200 μm, (b) 300 μm, (c) 5 μm.

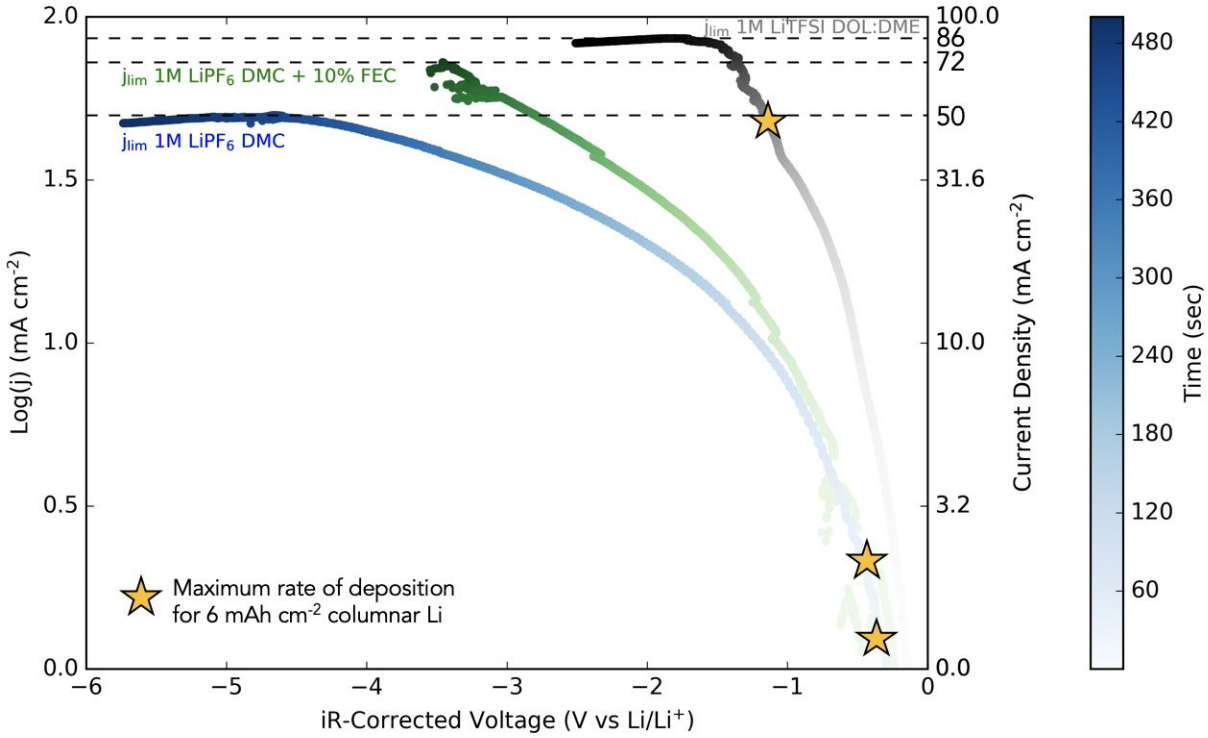


Figure S4. Linear sweep voltammetry from 0 V to -10 V vs reference Li for deposition on brass substrate in the three electrolytes, used to plot the depicted logarithmic current density on the y-axis (mA cm^{-2}) and iR-corrected voltage (V vs Li/Li^+) on the x-axis. iR-correction was done by using the ohmic resistance calculated by EIS, as shown in Figure S5. As shown, the current

densities for columnar growth in all three electrolytes is below their respective maximum current densities.

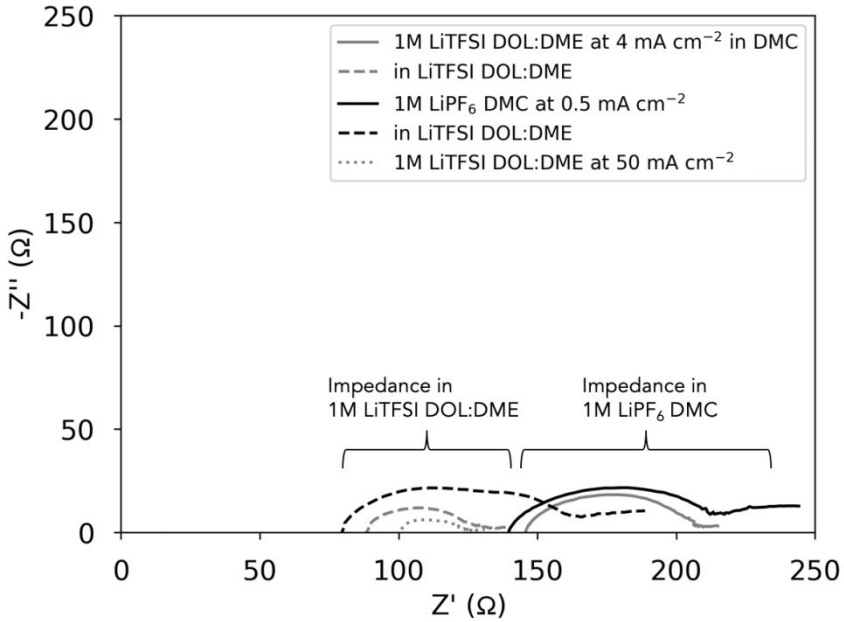


Figure S5. Columnar Li deposited in either 1M LiTFSI DOL:DME (gray) or 1M $LiPF_6$ DMC (black), with subsequent electrochemical impedance spectroscopy in either 1M LiTFSI DOL:DME or 1M $LiPF_6$ DMC (solid). Frequencies ranged from 100 kHz to 0.01 Hz, with voltage amplitude of 0.1 mA and 14 points per decade. The x-intercept of the high frequency indicates the ohmic resistance, this indicates that 1M LiTFSI DOL:DME has lower ohmic resistance than 1M $LiPF_6$ DMC.

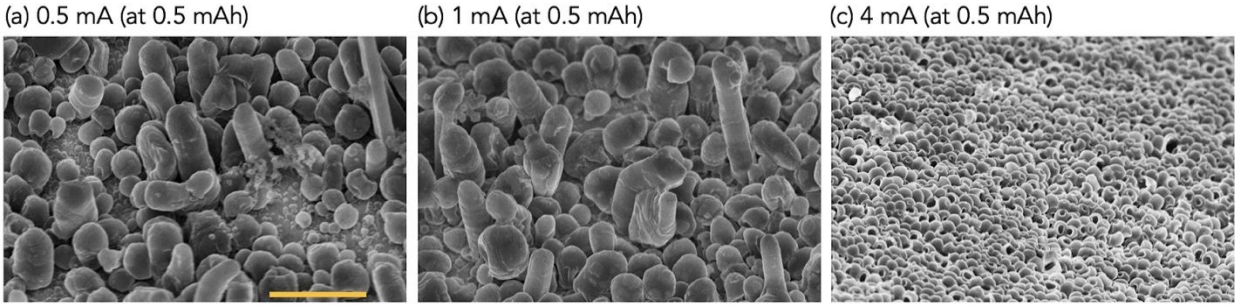
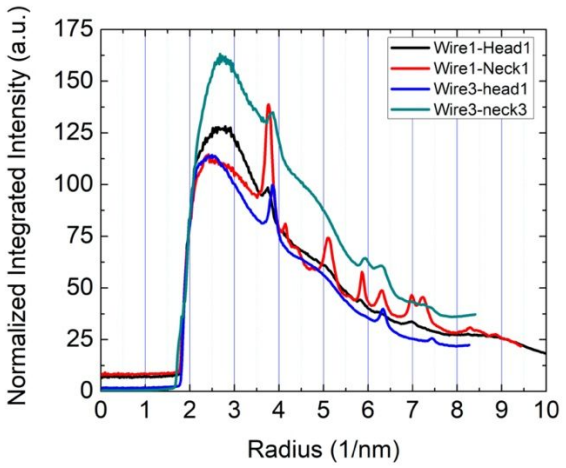


Figure S6. Deposition in 1M LiTFSI DOL:DME at (a) 0.5 mA cm^{-2}, (b) 1 mA cm^{-2}, and (c) 4 mA cm^{-2}. All plating tests were done with a total plating capacity of 0.5 mAh cm^{-2}. Scale bar corresponds to 5 μm.



Wire1-head1	D-spacing (Angstrom)	Li	LiF	Li_2O	Li_2O_2	Li_2CO_3	$LiOH*H_2O$
1	2.65			Li_2O(111)		Li_2CO_3(-112)	$LiOH*H_2O$(220)
2	2.38		LiF (111)				
3	1.7						
4	1.58				Li_2O_2(110)		
5	1.43	Li(211)	LiF(220)				
6	1.2				Li_2O_2(203)		
7	1.15		LiF(222)				
8	1.1	Li(310)			Li_2O_2(204)		

Wire1-neck1	D-spacing (Angstrom)	Li	LiF	Li_2O	Li_2O_2	Li_2CO_3	$LiOH*H_2O$
1	4.22					Li_2CO_3(110)	
2	2.65			Li_2O(111)		Li_2CO_3(-112)	$LiOH*H_2O$(220)
3	2.4		LiF (111)				
4	1.95						$LiOH*H_2O$(-301)
5	1.78	Li(200)					
6	1.7						
7	1.58				Li_2O_2(110)		
8	1.43	Li(211)	LiF(220)				
9	1.37			Li_2O(311)			

Wire3-head2	D-spacing (Angstrom)	Li	LiF	Li_2O	Li_2O_2	Li_2CO_3	LiOH or $LiOH*H_2O$
1	2.63			Li_2O(111)		Li_2CO_3(-112)	$LiOH*H_2O$(220)
2	2.56				Li_2O_2(101)		
3	2.38		LiF (111)				
4	1.67						
5	1.58				Li_2O_2(110)		
6	1.34				Li_2O_2(105)		

Wire3-neck3	D-spacing (Angstrom)	Li	LiF	Li_2O	Li_2O_2	Li_2CO_3	LiOH or $LiOH*H_2O$
1	2.86					Li_2CO_3(002)	
2	2.78						LiOH(101)
3	2.58				Li_2O_2(101)		
4	1.69						
5	1.6					Li_2CO_3(-130)	
6	1.56				Li_2O_2(110)		
7	1.42	Li(211)	LiF(220)				
8	1.33				Li_2O_2(105)		

Figure S7. Diffraction peak indexing using normalized integrated intensity. Peak positions from reference JC-PDS Catalogue #45-1460 (for LiF), #15-0401 (for Li), #09-0359 (for Li_2CO_3), #25-0486 (for $LiOH*H_2O$), #12-0254 (Li_2O). For Figure 5, growth asperities at 2 mA cm^{-2} in 1M $LiPF_6$ DMC.

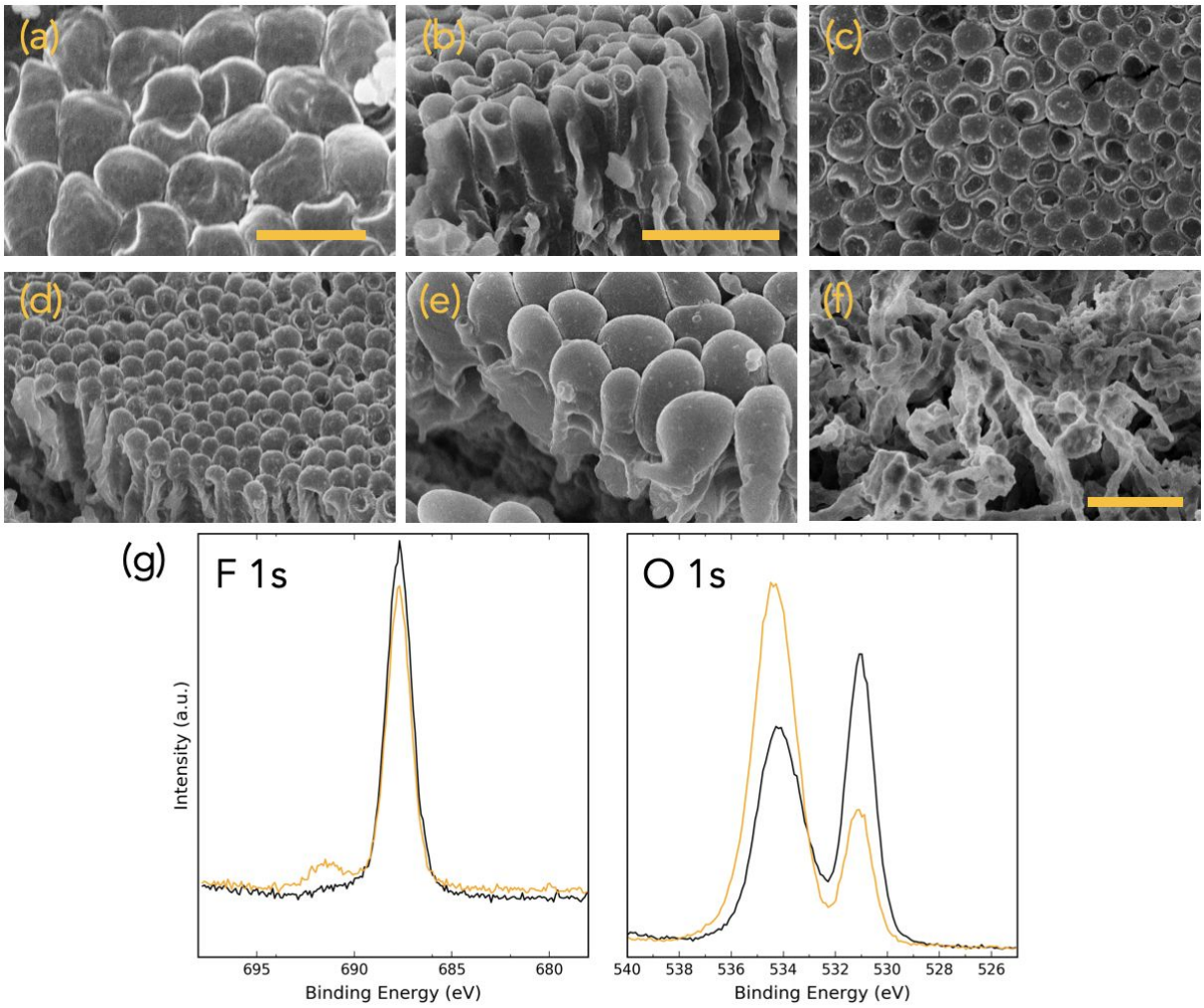


Figure S8. Plating in 1M LiTFSI DOL:DME at (a) 16 mA cm^{-2}, (b) 20 mA cm^{-2}, (c) 24 mA cm^{-2}, (d) 40 mA cm^{-2}, (e) 50 mA cm^{-2}, and (f) 60 mA cm^{-2}, for a total of 2 mAh cm^{-2} (10 μm thickness). (g) Corresponding XPS point scans for F 1s and O 1s scans, with black curves representing uniform plating at 4 mA cm^{-2} and orange curves representing non-uniform plating at 60 mA cm^{-2}.

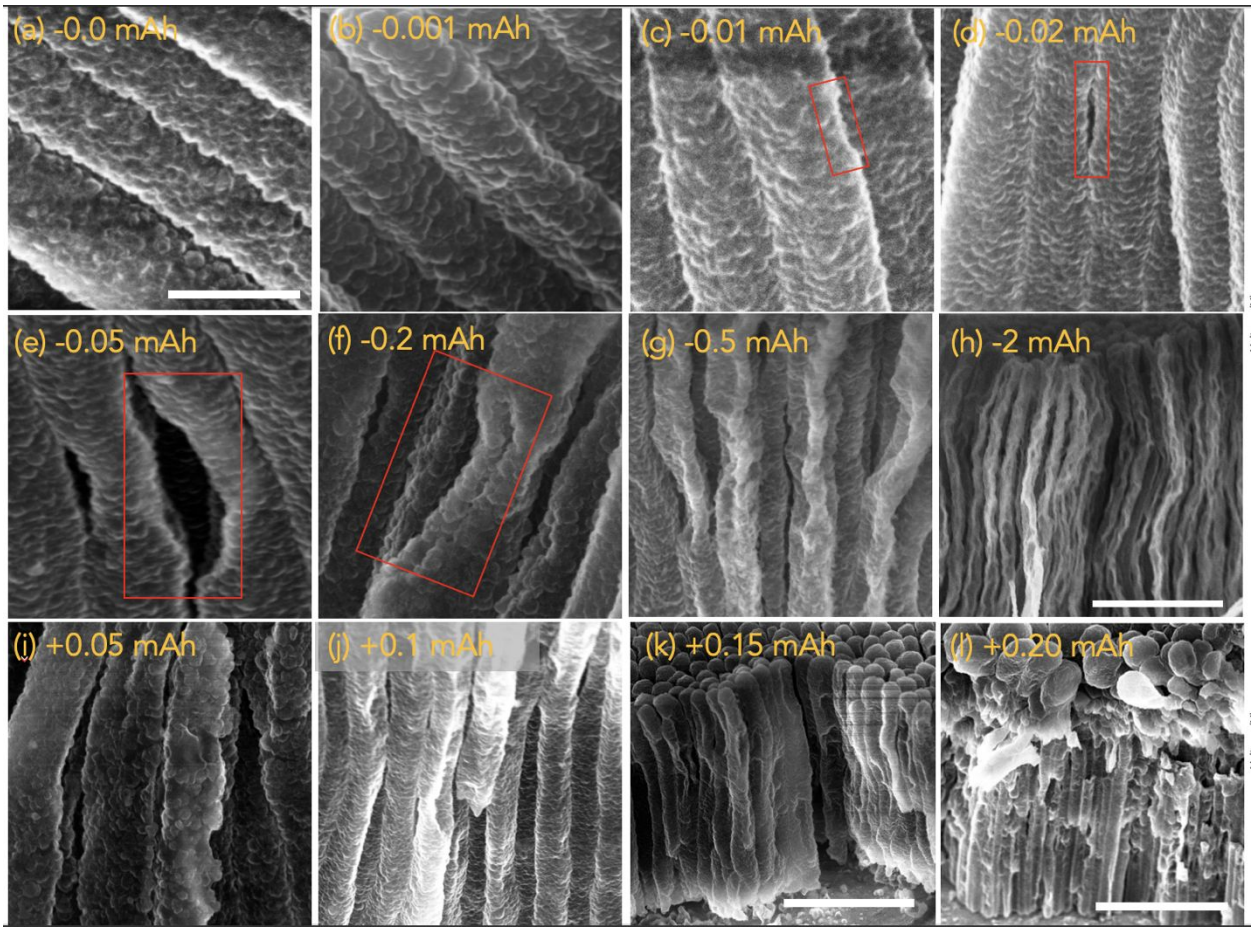


Figure S9. High resolution images of cross-sectional view during stripping and replating, after initial plating of 0.5 mA cm^{-2}, 1 mAh cm^{-2} columnar lithium. After initial plating of columnar lithium, stripping indicates that the thickness/height of the deposits does not change. Rather, lithium is stripped from various locations along the column, indicating a high electrochemically active surface area along the entire lengths of the columns. (h), (k), (l) scale bars correspond to 3 μm, all other subplot scale bars correspond to 500 nm.

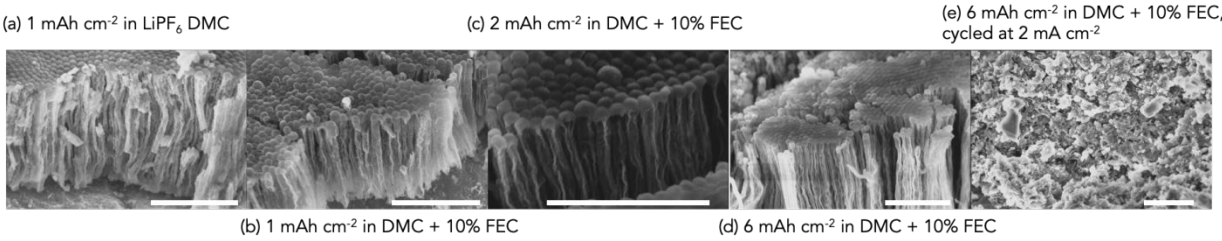


Figure S10. Post-mortem SEM images of (a) 1 mAh cm^{-2} plated columnar Li in 1M $LiPF_6$ DMC, (b) 1 mAh cm^{-2} plated columnar Li in 1M $LiPF_6$ DMC + 10% FEC, (c) 2 mAh cm^{-2} plated columnar Li in 1M $LiPF_6$ DMC + 10% FEC, (d) 6 mAh cm^{-2} plated columnar Li in 1M $LiPF_6$ DMC + 10% FEC, and (e) 6 mAh cm^{-2} plated columnar Li in 1M $LiPF_6$ DMC + 10% FEC and cycled at higher current of 2 mA cm^{-2}, 1 mAh cm^{-2} (all other conditions were cycled at 0.5 mA cm^{-2}, 1 mAh cm^{-2}).