Supplemental info for

## Understanding the Critical Chemistry to Inhibit Lithium Consumption in Lean Lithium Metal Composite Anodes

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**Figure S1**) C1s XPS for pristine CNF showing the surface functionalization consists mostly of the C-C bond (284.8 eV).



**Figure S2)** High resolution SEM image of Li/CNF after 1mAh/cm<sup>2</sup> of Li electrodeposition at 0.05mA/cm<sup>2</sup> deposition rate showing the coating of Li on the CNF, changing the morphology from the smooth surface of the pristine CNF to one that is rigid and coated with Li metal.



**Figure S3)** Coulombic efficiencies for Li/CNF composite anodes with varying total areal capacities and cycled current rates  $1\text{mAh/cm}^2$  with no electrolyte additive cycled at 1C (**a**) and C/10 (**b**),  $1\text{mAh/cm}^2$  with VC (2 wt.%) at 1C (**c**) the rapid cell failure in which the active lithium is consumed is highlighted in the decline in the Coulombic efficiency, and C/10 rate (**d**), 2 mAh/cm<sup>2</sup> with VC at 1C rate (**e**) and C/10 rate (**f**), and 3 mAh/cm<sup>2</sup> at 1C (**g**) and C/10 (**h**)



Figure S4) Specific capacity v cycle number for Li/CNF composite with a deposition of  $1mAh/cm^2$  with no electrolyte additives.



**Figure S5**) Lithium retention discharge curves for 1 mAh/cm<sup>2</sup> with the addition of 2% VC Li/CNF composite with 622 NMC cathode, showing the formation of the "knees" that indicate the beginning of rapid loss of active lithium in the composite anode.



**Figure S6**) Lithium retention discharge curves for replicated full cells for 3mAh/cm<sup>2</sup> Li/CNF composite with 622 NMC cathode.



**Figure S7**) Specific capacity and CE of a retrieved cathode from a composite anode cell, after reaching a state of rapid cell failure. The cathode was used in a new cell with a fresh lithium metal anode and cycled to determine that the capacity fade in the CNF composite anode was not primarily due to the cathode.



**Figure S8**) (a) Specific capacity retention for the first 100 cycles comparing Li/Graphite composite anode against lithium metal and bare graphite anodes (b) Coulombic efficiency for Li/Graphite anode over 1000 cycles (c) specific capacity retention for 1000 cycles comparing Li/Graphite composite anode to bare graphite anode. All full cells utilize 622 NMC cathode.



**Figure S9**) SEM images for (**a**) Cross section of Li/graphite composite electrode after electrodeposition highlighting that lithium does deposit throughout and coats through the graphite particles and (**b**) surface morphology of Li/graphite composite electrode after 1000 cycles. Lithium metal is still present, but the surface morphology has changed to an overall rougher and more porous morphology.