# Supporting Information

## Experimental

*Synthesis of particle:* 200g of potassium polysulfides from Sigma Aldrich were dissolved in 1.5 liters of deionized water and mixed with 1g branched PEI (75k MW) and 2g Ketjen Black 600JD from Azko Nobel yielding a black solution. A clear solution of 400g ascorbic acid dissolved in 2 liters deionized water was slowly added to this mixture. The color of the reaction mixture changed during addition from dark black to slightly yellow, then bright yellow, followed by gradual darkening to a dark soft grey/blue. The reaction was allowed to proceed for 4 hours after which it was centrifuged (~800 rpm in a RC 12BP centrifuge from Thermofisher) and rinsed once in 1–liter deionized water.

*Layer by layer coating of the particle:* 5 layers of branched PEI/Cloisite clay were adhered to the particle to yield the finished sulfur truffle active material. Branched PEI (75k MW) was added first and last. Each layer addition was performed by suspending the particle mass in 1 liter of deionized water with stirring, adding $LiNO_3$ to obtain a 0.1 M concentration and then adding 1g branched PEI or 1 g Cloisite clay as needed to build the layer to layer membrane. The second layer was always polystyrene sulfonate (PSS) to ensure conformal film growth. Each layer solution was allowed to mix for 1 hour. One rinse in 1–liter deionized water after each layer ensured the removal of excess, unadsorbed material. The product was then dried in the oven, under vacuum at 80 degrees Celsius as needed to dry (1-2 days), followed by TGA analysis to determine the sulfur content (typically 85%–90%).

*Cathode powder preparation:* The dry active material was ground with a pestle and mortar and mixed with the desired ration of a 1:1 SuperPLi and carbon nanofibers, then dry ball milled with small beads at low energy (100 rpm in a Fritsch Pulverisette 7 ball mill) for 2 hours. This step ensures the adhering of the SuperpLi dots to the sulfur truffle membrane with long range connections supplied by the carbon nanofibers. For example, 0.3g active material is mixed with 0.0974g SuperPLi and 0.0974g carbon nanofibers (Sigma Aldrich) (ratio of 57/37/6 of active material/carbon/binder). 40g small beads are added to the ball mill cup.

*Cathode slurry preparation:* A small ratio (1–10%) of a binder such as Nafion is mixed well with the cathode powder described above. The mixing is done by hand with pestle and mortar. Water is used to make the slurry which is further homogenized in a Thinky ARE–310 centrifugal mixer at 2000 rpm. For example, 0.632 ml of a 5% Nafion solution is added to the active material/carbon mixture described above in a mortar. 1 additional ml of water solvent is added and mixed well with the pestle to form a thick paste then transferred (scooped) to a 9 ml Teflon Thinky cup. An additional 3 ml water are added then the slurry is mixed for 10 minutes at 2000 rpm in the Thinky mixer.

*Slurry casting/calendering on aluminum foil:* The slurry is poured/scooped onto aluminum foil and cast with 1000 µm wet gap then dried in vacuum oven at 80 degrees Celsius for at least 4 hours. The dry cathode is then calendered down to 85 µm in thickness in a hot press (80 °C).

*Coin cell preparation:* Disks with an area of 2.835 $cm^2$ are stamped out, weighed and placed on the bottom can of the coin cell inside the glovebox. A thick, fiber glass separator BGO21565 or BGO28065 from Hollingsworth & Vose was placed on top then 0.21 ml electrolyte was pipetted into the separator. A pre-conditioned lithium disk (1.911 $cm^2$) was placed on top, followed by a 0.5 mm spacer, a spring and the top cover. The coin cell was then crimped and tested. The electrolyte used was a solution of 1 M LiTFSI, 0.02 M $LiNO_3$ in 1:1 DOL:DME. A typical open circuit potential of 2.8 V to 3.1 V is observed with an impedance below 100 Ω $cm^2$. Capacities are calculated based on the mass of sulfur which corresponds to the limiting area of the lithium metal anode (1.911 $cm^2$).

*Pre-conditioning of the lithium metal foil:* In a glovebox, mix 1mmol (0.0459 g) $Li_2S$ with 0.625mmol (0.1603g) $S_8$ (elemental sulfur) in 20 ml of a 1:1 solvent mixture of glyme and dioxolane (DME:DOL) according to the following reaction:

$$8Li_2S + 5S_8 \rightarrow 8Li_2S_6$$

The expected product is ~0.05 M lithium polysulfide mixture. The mixture was allowed to react with vigorous stirring at room temperature for several days (inside the glovebox). It took several hours for the reaction to start producing the brown polysulfide color. Pre-conditioning was achieved by immersing a freshly scraped lithium disk in ~0.5 ml polysulfide solution for at least 1 hour and no longer than 1 week. The treated lithium disk was rinsed with THF, glyme or dioxolane as needed to remove the excess polysulfide solution then allowed to dry for 2 to5 minutes.

*Lithium deposition:* Lithium was deposited on a copper substrate with or without polymer artificial SEI in a 2032 coin cell. The lithium source was a lithium disk 1.911 $cm^2$ in surface area or a $LiFePO_4$ electrode 2.011 $cm^2$ in surface area. Deposition from the lithium disk was limited to ~1.5 $mAh/cm^2$ while deposition from $LiFePO_4$ electrodes was not limited. Typical lithium loading in these electrodes was 2-2.5 $mAh/cm^2$. A fiber glass separator BGO21565 or BGO28065 from Hollingsworth & Vose was used on with 0.21 ml electrolyte.

*Fabrication of multilayer artificial SEI:* Multilayers were built on an inverted copper substrate with a surface area of 2 $cm^2$ using a Nanostrata robot. The substrate was spun and immersed in a dilute polymer solution of a positively charged polyelectrolyte such as PAH or PDAD for 20 minutes. Three 30 second rinses followed after which the substrate was dried with nitrogen for 30 seconds. Next the substrate is immersed (for 20 minutes) into a dilute solution of a negatively charged polyelectrolyte such as PEDOT:PSS or Montmerillonite/Cloisite clay. Three 30 second rinses were followed by 30 second nitrogen drying time segments. All polymer solutions contain 0.1 M $LiNO_3$ and are below 10 mM in polymer concentration. Rinse solutions also contain 0.1 M $LiNO_3$. The PEDOT:PSS polymer solution was prepared by diluting 0.1 ml of 1% stock PEDOT:PSS solution to 100 ml. 0.1 g clay was suspended in 100 ml deionized water solution with stirring. All polymers and salts were purchased from Sigma Aldrich. After assembly, the nanomembrane coated substrate was inserted in a pH = 10 solution (prepared with sodium hydroxide) for 5 hours, rinsed well then dried under vacuum in an oven at a temperature of 70 ˚C for 2 hours. This procedure was first introduced earlier.[35]

*TEM data acquisition and processing:* Lacey carbon grids with membrane-wrapped sulfur particles were imaged under cryogenic condition using Titan Krios transmission electron microscope (FEI, Hillsboro, Oregon) operated at 300 kV. Images were first collected at 2200x magnification to assess the sample distribution. Single axis tilt series were then collected in a 2° increments from -68° to +68° at 11000x magnification (pixel size 3.3 Å) with a 4 µm defocus and a total dose of ~500 e-/A2. Images were recorded on a DE20 direct electron detector camera (Direct Electron, San Diego, CA) in integrating mode. The resulting tilt series were processed with automatic alignment tool from TomoJ plug-in of ImageJ.[36] The tilt series were binned by 4 and reconstructed using weighted back-projection method as implemented in TomoJ. The 3D volume was visualized in UCSF Chimera for generating 2D projections and recording the movie.[37]

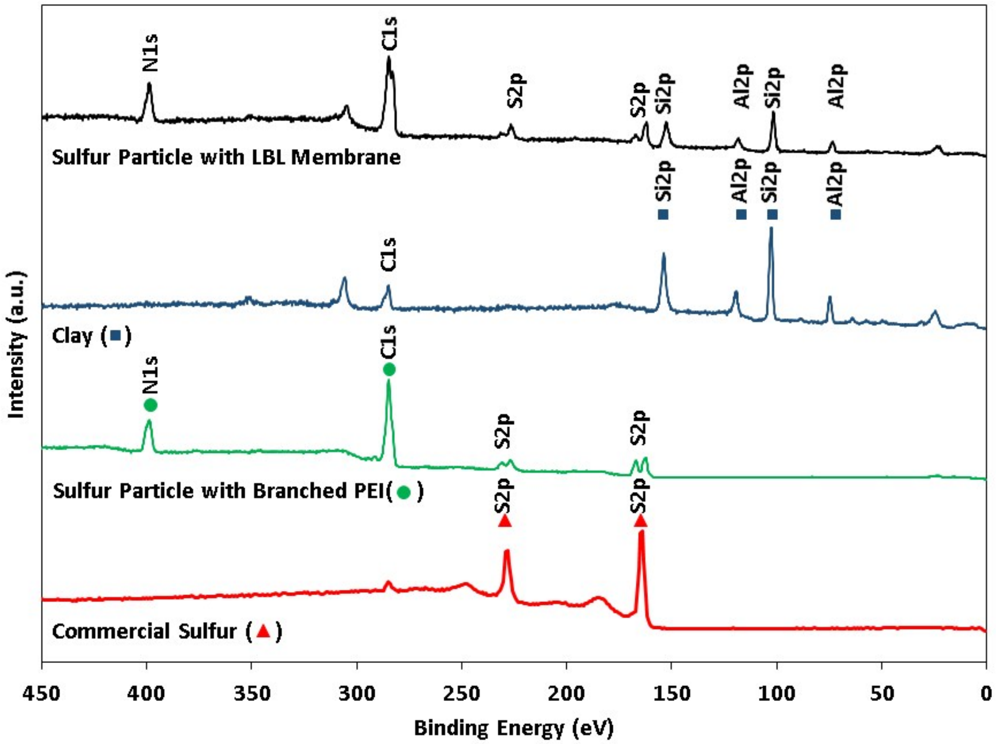

Figure S1. XPS spectra of commercial sulfur (red), sulfur coated with branched PEI (green) identified by N1s peak, clay (i.e. Al2p and Si2p) (blue), and sulfur coated with LBL membrane (black).

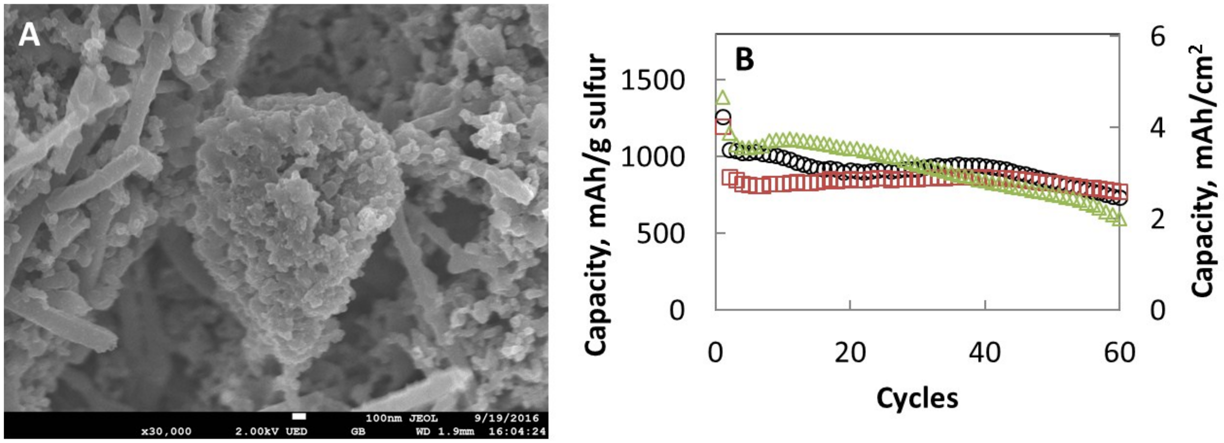

Figure S2. (A) SEM image of sulfur particle in the finished cathode (SEM – A) where it is wrapped in polymer/clay layers and is covered in conductive carbon. (B) Effect of binder on cycle life of high loading dense sulfur cathodes. The cathode content ratio is 65/25/10 (active material/carbon/binder) and the binder varies between Nafion (green triangles), branched PEI (black circles) and PAMPS (red squares). The operating rate is 1 mA/cm$^2$ with full discharge in ~4 hours.

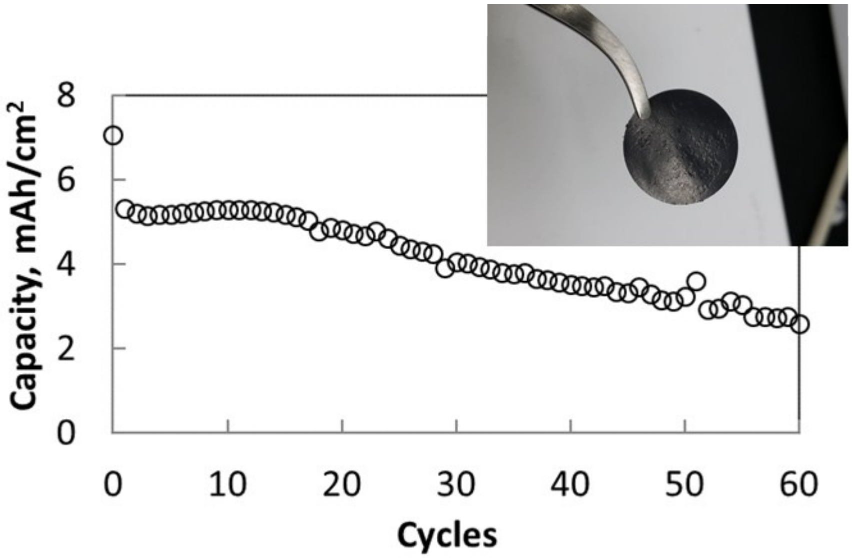

Figure S3. A 100 µm thick freestanding sulfur cathode cycled vs. a lithium metal anode. The cathode measures 19 mm in diameter and weighs ~40 mg. It consists of 80% sulfur active material, 10% conductive carbon additive and 10% flexible polymer. The effective charge/discharge rate is C/4.

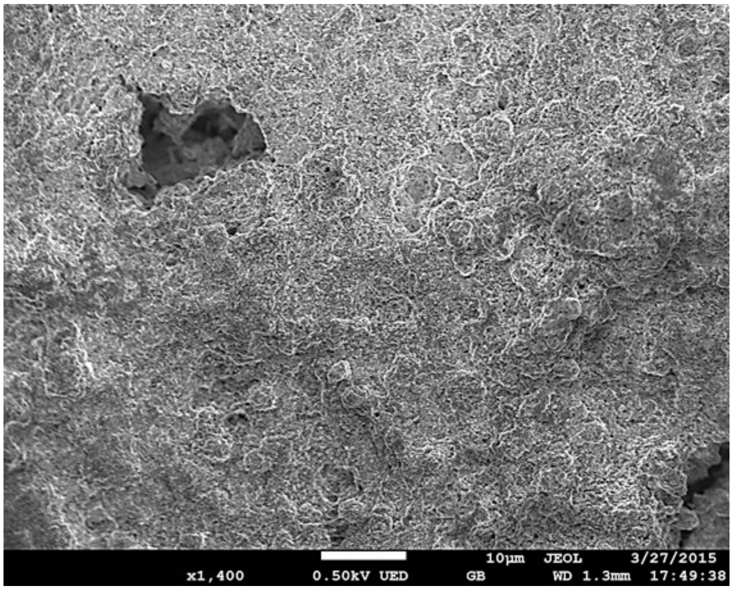

Figure S4. SEM image of the uniform sulfur coating on top of the conductive carbon which occurs in the event of polysulfide dissolution.

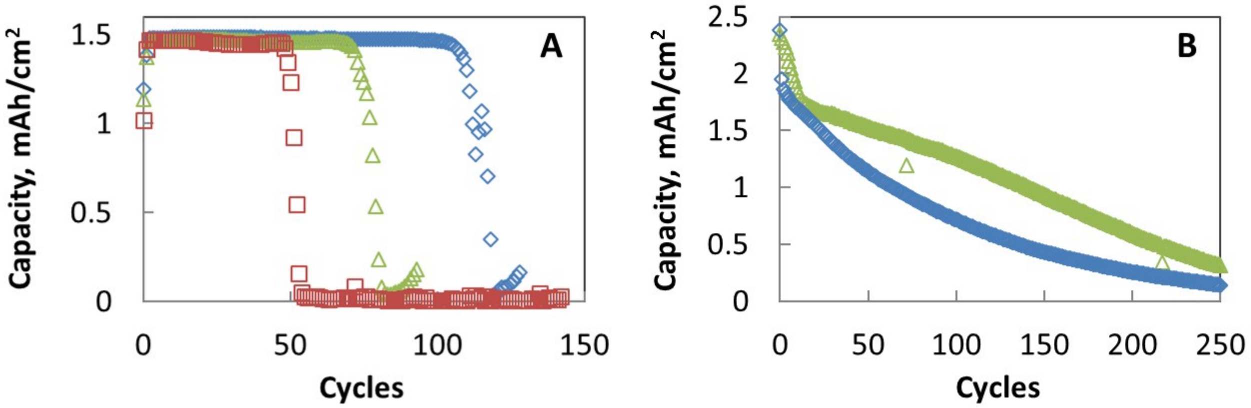

Figure S5. (A) Stable cycles of lithium deposition/stripping at various current rates in a 2032 coin cell from a lithium metal foil onto a copper counter. 1 mA/cm$^2$ offers over 100 stable cycles (blue diamonds), 2 mA/cm$^2$ offers 70 stable cycles (green triangles) and 4 mA/cm$^2$ offers 50 stable cycles (garnet squares). The coulombic efficiency in all cases remains high for a certain number of cycles dependent on the current rate after which it drops precipitously. In all cases, once the drop in stripping efficiency commences, no stripping is possible after less than 10 cycles. (B) Cycling of $LiFePO_4$/copper with 1 M LiTFSI, 0.02 M $LiNO_3$, in DOL:DME 1:1 solvent mixture. A polymeric/inorganic layer by layer reinforcement ($(PAH/PSS)_4$+$(PEDOT:PSS/PDAD)_{11}$+$(Cloisite/PDAD)_4$) for the SEI is deposited on the copper counter (green triangles) which improves the amount of lithium recovered on each cycle if compared with the unprotected copper (blue diamonds). All the lithium in the $LiFePO_4$ cathode is utilized on each cycle (full discharge) which makes this limited lithium source a very tough and clear test for the coulombic efficiency of the deposition/dissolution of lithium on the copper counter “anode”.

## References

[1] C. B. Bucur, A. Lita, N. Osada, J. Muldoon, *Energy Environ. Sci.* **2016**, *9*, 112–116.
[2] C. Messaoudil, T. Boudier, C. O. S. Sorzano, S. Marco, *BMC Bioinformatics* **2007**, *8*, 288.
[3] E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng, T. E. Ferrin, *J. Comput. Chem.* **2004**, *25*, 1605–1612.