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# Supporting Information

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Supporting Information

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## 1. Experimental Section

***Preparation of nanomaterial suspensions***: The titania NP (~30-50 nm, 99% purity, Rutile, Advanced Materials$^{TM}$), MWCNT (>95% carbon, L: 6-9 nm x 55 μm, Sigma Aldrich) and PANI (~3 μm, average $M_w$ >15,000, emeraldine salt, Sigma Aldrich) suspensions are prepared using pure ethanol (Decon, 200 Proof) and selections of materials above (1wt%). After mixing the particles with pure ethanol, all the suspensions are sonicated for 10 minutes to allow good dispersion of particles.

***Preparation of PEISC and VISC****:* PEISC – The sulfur is infused to PEI attached MWCNT matrix as described in previous report [1]. The S@C composite (80 wt%) was mixed with Super P (10 wt%) and polyvinylidene fluoride (10 wt%) dissolved in N-methyl-2-prolidone (15 wt%) in N-methyl-2-prolidone, and the mixture is ball-milled at 50 rev $s^{-1}$ for 30 minutes. The resulting viscous slurry was coated onto a carbon sprayed aluminum foil as a current collector using doctor-blade method. The coated slurry is then dried in a convection oven at 60 °C for 5 hours. The prepared electrode (1.2 mg $cm^{-2}$ S & 50% S) is cut into a circular disk. VISC – sulfur was vapor-infused into the carbon fiber matrix via high temperature method [2]. The S@C composite (85 wt%) was mixed with vapor grown carbon fiber (10 wt%) and polyvinylidene fluoride (5 wt%) dissolved in N-methyl-2-prolidone (15 wt%) in N-methyl-2-prolidone, and the mixture is ball-milled at 50 rev $s^{-1}$ for 30 minutes. The sulfur cathodes (3.5 mg $cm^{-2}$ S and 68% S) are prepared by coating the composite onto a carbon sprayed Al foil. Including coating materials of the laminated PANI, the sulfur contents for PEISC (43% S) and VISC (63% S) are achieved. The cathode size (1.266 $cm^2$) is used for the cathodes. Including the weight of the coating materials for laminated PANI separator, the sulfur content for VISC and PEISC are 63% and 43%, respectively.

***Coating Process****:* Separator (Celgard 2500) is cut into a circular disk (1.6 cm diameter). A cover glass (1.8 by 1.8 cm) is used as a substrate for the cutted separators. The separator is placed on top of the cover glass and the edges of the separator is taped with

Kapton tape. LBS method requires tap water, prepared suspensions, a beaker, and micropipette. Prepared separator is quickly rinsed with running water. The suspension (<1mL) is injected at the surface water via a neck of the beaker. During the self-assembly process, the separator is slowly raised followed by constant injection of the suspension (See supplementary videos). After single coating layer of desired material is coated on the separator, the coated separator is then dried on a hotplate (110 $^{o}$C) for less then a minute. After coating a single layer, a drop of isopropanol (IPA) is applied to the coated separator to uniformly wet the surface with water, and the separator is remained in clean water about 10~20 seconds. After fully wetting the coated separator, another LBS coating is performed until desired number of layers and materials are coated. After desired numbers of coatings are achieved, the separator is dried on the hotplate (125 $^{o}$C) for 1 minute to fully remove any moisture on the separator. To fabricate the laminated PANI structure, single coating of MWCNT is applied on the separator. After drying, a drop of IPA is used to fully wet the separator surface and remained inside of the clean water ~15 seconds. After MWCNT coating, 2 coatings of PANI are made on the separator followed by 3 coating layers of titania NP and ending with another layer of PANI. Each coating methods is same as mentioned above to coat these materials. After the final drying, the separator is removed from the cover glass substrate and used to fabricate Li-S cells.

*Battery assembly:* CR2032-type coin cells are used to make Li-S cells. Prepared separators, Li foil disks (0.5 inch in diameter), prepared cathodes, stainless-steel springs and spacers, and the electrolytes (40 μL, 1M Bis(trifluoromethane)sulfonamide lithium salt (LiTFSI, Sigma Aldrich) in DME:DOL (1:1 v/v) electrolyte with/without 0.05M $LiNO_3$) are used to assemble Li-S cells. First, electrolyte (20 μL) is applied onto coated side of the separator, and cathode is placed on top of the separator. Then, another half amount of the electrolyte is applied at the other side of the separator, and Li foil is placed. On top of the Li, stainless steel disk is placed, and the spring is placed next. After all the components are assembled, the coin cell is punched (15 MPa). The cell is rested around 15 minutes before testing. The assembly process is carried out in Ar filled gaseous environment (MBraun Labmaster).

***Characterization**:* The assembled Li-S cells are tested at room-temperature and evaluated under galvanostatic conditions using Neware CT – 3008 battery testers. Two voltage windows are chosen for Li-S systems that involve $LiNO_3$ co-salt in the electrolyte. Without the co-salt, 1.5V to 2.6V voltage window is chosen whereas with the co-salt, 1.7V to 2.6V voltage window is chosen to prevent the degradation on the passivation layer formed by $LiNO_3$ at the surface of Li. Cyclic voltammetry measurements are done by CHI600D potentiostat, and scan rate (0.1 mV $s^{-1}$) and voltage window (1.5V to 3V) is used during the analysis. LEO 1550 FESEM is used for SEM and EDXS analysis with 5 kV and 10 kV acceleration voltages. AC impedance spectroscopy is measured using Novocontrol N40 broadband dielectric spectroscopy. KSV NIMA L & LB Troughs equipment is used to characterize the films qualities and measure surface pressure profiles of the materials. The trough (7.5 cm x 32.4 cm, See Figure S1) is cleaned using pure ethanol and DI water to rinse off all contaminants. The trough is filled up with DI water. For LBT measurement, suspension (~3 mL) is spread at the surface of water and rested about 5 to 7 minutes to evaporate remaining ethanol from the suspension. The floating particles are compressed via mechanical barriers (3 mm $min^{-1}$) and the surface pressure profiles are measured. For LBS measurement, the trough area (~25 $cm^2$) is matched with the side of the beaker to compare actual coating process. The surface pressure profile is measured during the self-assembly process, and the fully formed films are compressed (3 mm $min^{-1}$) without resting to collect the full profiles.

## 2. Supporting Figures

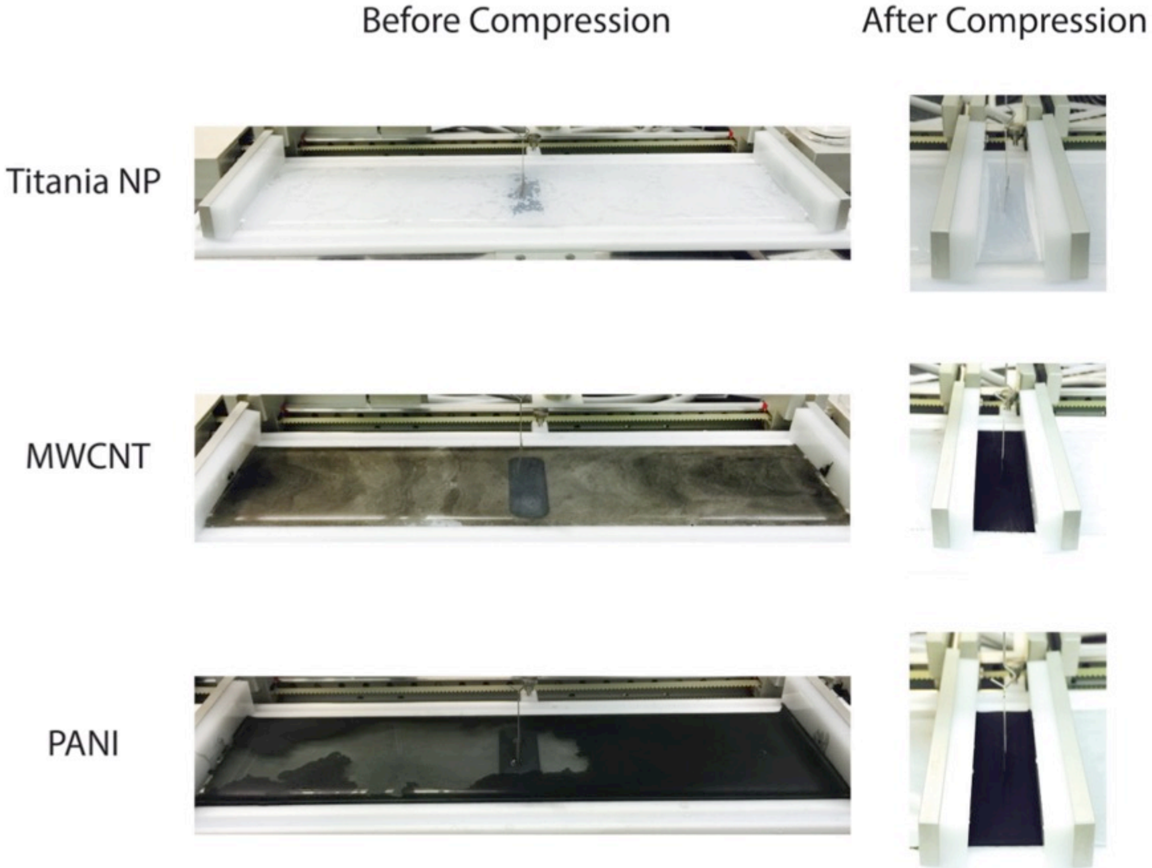

**Figure S1.** Physical images of Langmuir-Blodgett trough surface pressure profile measurements before and after the compression of the films of Titania NP, MWCNT, and PANI. Note that folding of the films, starting at the mechanical barriers, is shown in "After compression" which indicates that films are stable at liquid-gas interface.

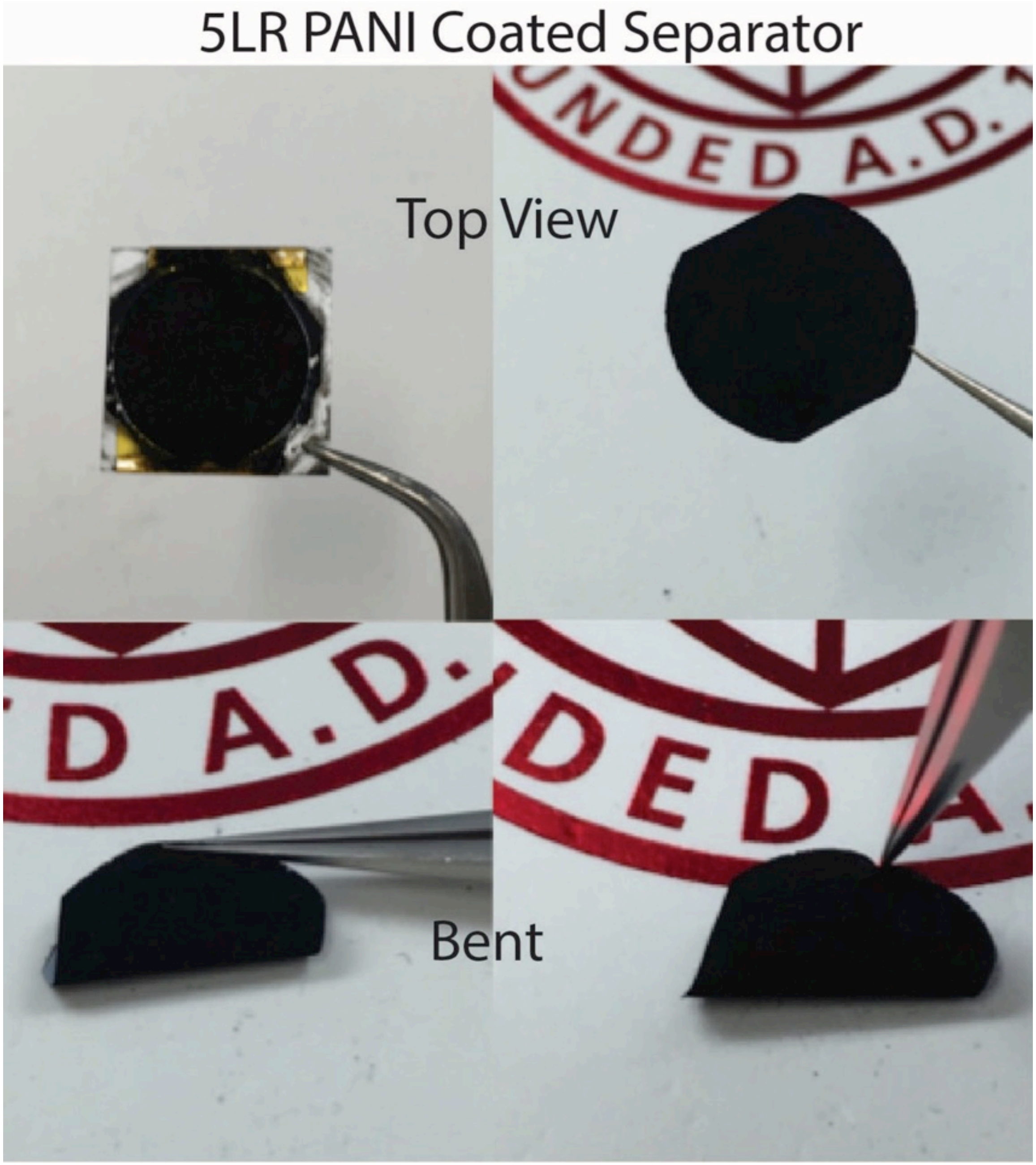

**Figure S2.** Mechanical strength demonstration of 5LR PANI coated separator.

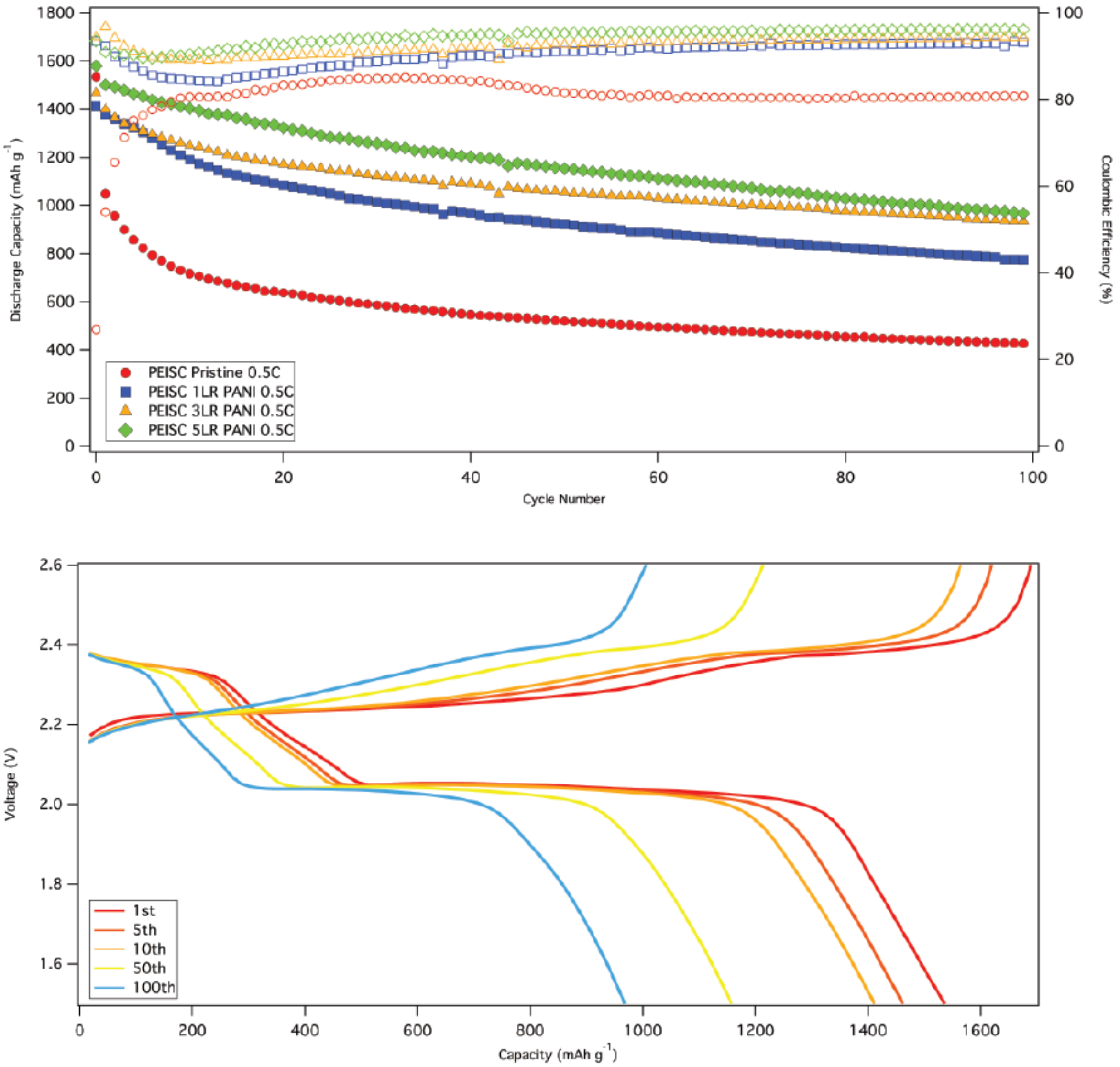

**Figure S3.** Cycling performance of the 1-5LR PANI coated separators and pristine separator with PEISC and no $LiNO_3$ in the electrolyte Li-S cells at 0.5C for 100 cycles and the voltage profiles of 5LR PANI coated separator Li-S cell at 0.5C for various cycles.

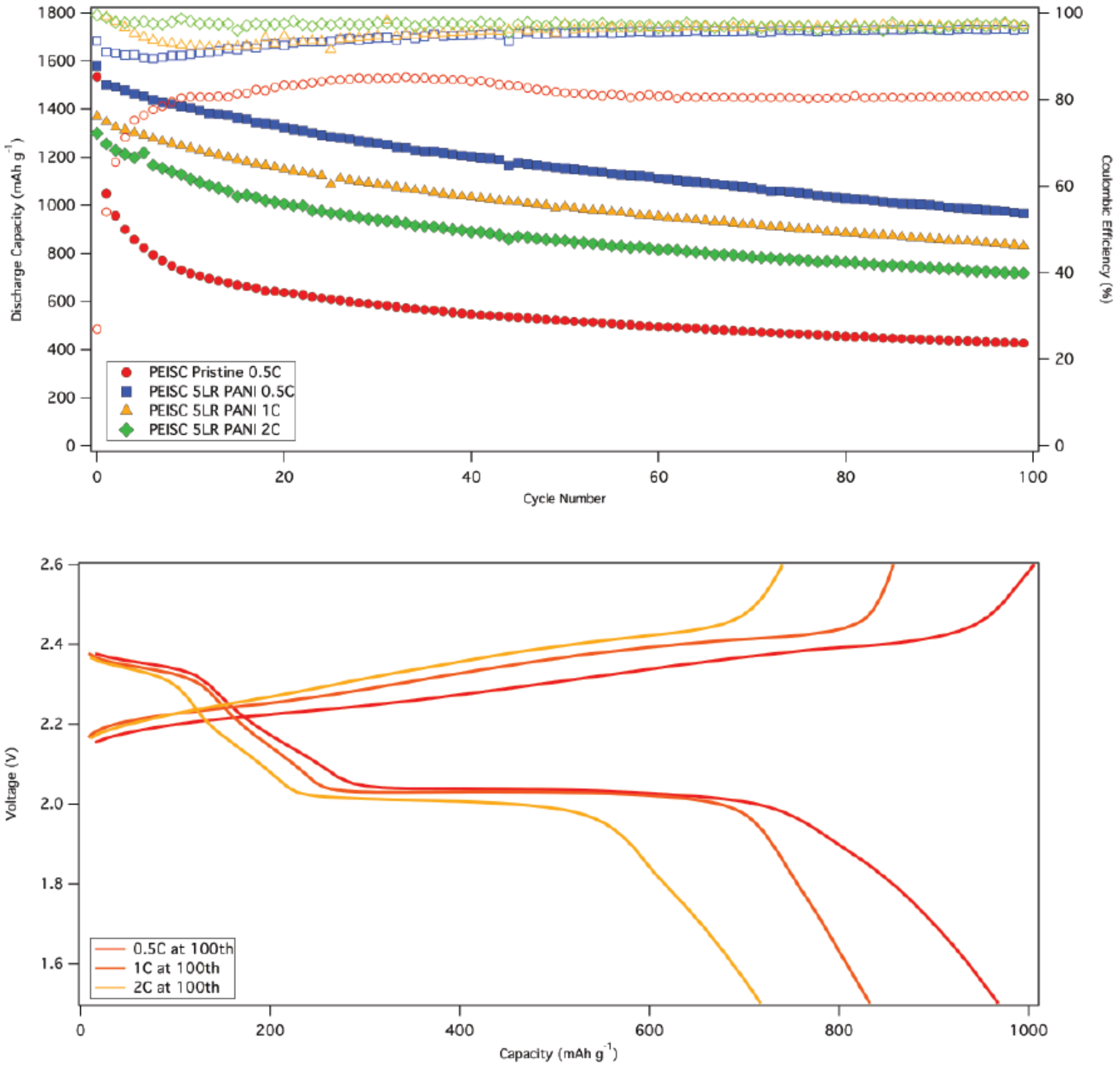

**Figure S4.** Cycling performance of 5LR PANI coated separators and pristine separator with PEISC and no $LiNO_3$ in the electrolyte Li-S cells for 100 cycles at three different C rates and the voltage profiles of 100th cycled 5LR PANI coated separators with PEISC Li-S cells at three different C rates for various cycles.

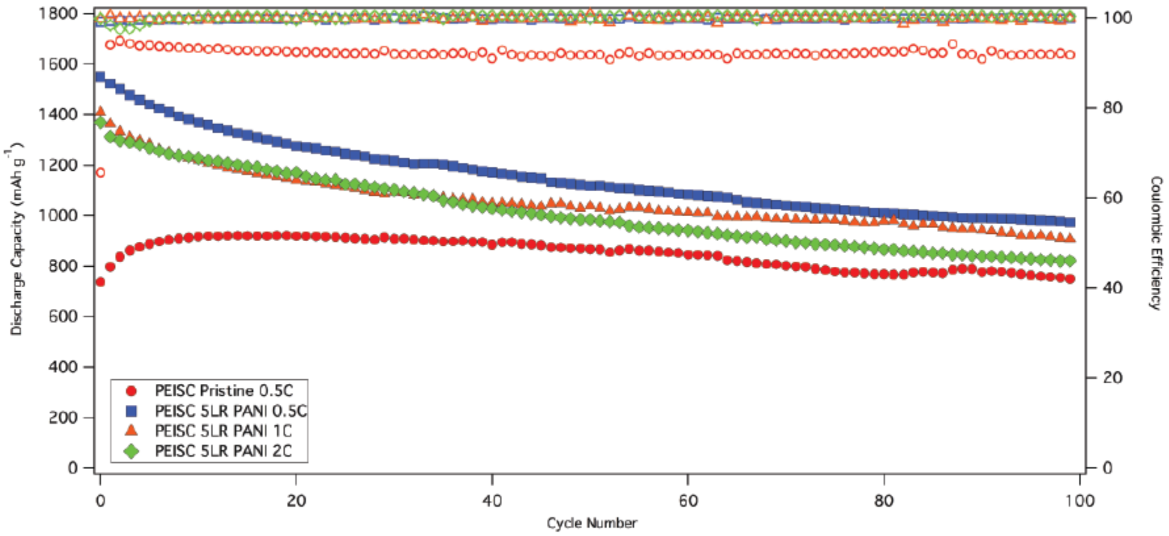

**Figure S5.** Cycling performance of 5LR PANI coated separators and pristine separator with PEISC and 0.05M $LiNO_3$ in the electrolyte Li-S cells for 100 cycles at three different C rates.

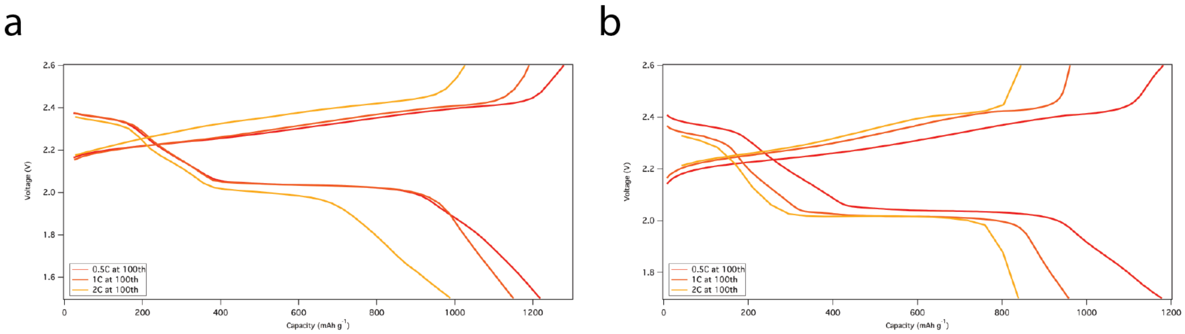

**Figure S6.** (a) Voltage profiles of the laminated PANI separator with PEISC and without $LiNO_3$ in the electrolyte Li-S cells at 100th cycle for three different C rates. (b) Voltage profiles of the laminated PANI separator with PEISC and with 0.05M $LiNO_3$ in the electrolyte Li-S cells at 100th cycle for three different C rates.

# After 100th Discharge

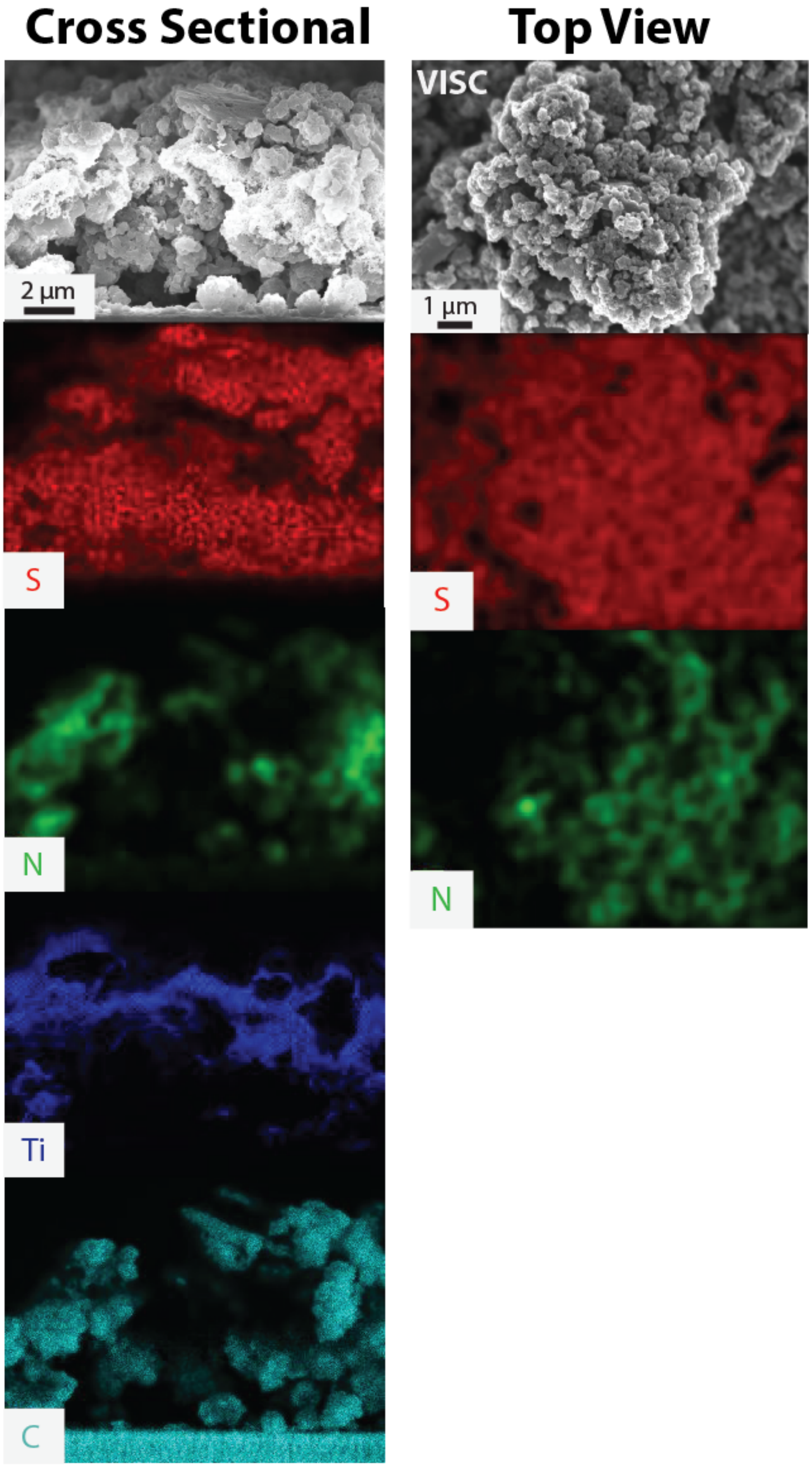

**Figure S7.** SEM and EDXS (Cross sectional elemental mapping: Sulfur, Nitrogen, Titanium, and Carbon & Top-view elemental mapping: Sulfur and Nitrogen) of the cycled laminated PANI separator with VISC.

## References

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[2] N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, L. A. Archer. *Angew. Chemie* **2011**, 50**,** 5904–5908.