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Electronic Supplementary Information

Experimental Methods

Synthesis of selenium particles: 1.2g of selenium was refluxed with 12g sodium sulfite (Na_2SO_3) in 65 mL water. 31g ascorbic acid was dissolved in 140 mL water and mixed with 19.5 mL polymethacrylic acid (PMA). This solution is diluted to a total of 265 mL and added to the selenium solution. A pH of 5.1 is observed and a dark garnet color. The solution is allowed to stir for 24 hours during which the color becomes milky garnet. Similar results can be obtained if oxalic acid, HCl or a 3:1 mixture of H_2SO_4 and HNO_3 (this acid mixture is used to functionalize Ketjen black carbon as previously reported²¹) are used as acids instead of ascorbic acid. The reaction pH needs to be maintained between 4 and 6. Other polymers can be used instead of PMA, such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), branched polyethylene imine (bPEI), polyvinylpyrrolidone (PVP), Nafion, polystyrene sulfonate (PSS), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) or poly(diallyldimethylammonium chloride) (PDAD) or others.

Synthesis of sulfur/selenium hybrids: 12g of sodium sulfite (Na_2SO_3) and 1.2g selenium have been refluxed and stirred for several hours in 80 mL water (boiling). This reaction yields a Na_2SeSO_3 solution. 1g of ball milled Ketjen black has been added to a 1L volume containing a 3:1 ratio of concentrated sulfuric acid:nitric acid and refluxed and stirred at 70 degrees for at least 1 hour. The 80 mL Na_2SeSO_3 solution was mixed with 50g sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and 5 mL of a 1% solution of conductive grade PEDOT:PSS and mixed in a 3.5 liter volume of water with vigorous stirring. To this mixture, 80 mL of Ketjen black acid solution (Ketjen black refluxed in a 3:1 mixture of H_2SO_4 and HNO_3) is rapidly added and stirred vigorously for at least 24 hours. Color should change from black to beige. High excess of oxalic acid can also be used instead of inorganic acids. After the reaction completes and stirring is stopped, product particulates can sediment to the bottom of the reaction beaker over several hours. (centrifugation can also be used to collect the reaction product) If needed, several rinses in distilled water may be necessary to remove excess carbon and polymer. This can be achieved by using a vortex mixer and a centrifuge.

Layer by layer coating of the particle: selenium particles were wrapped with a polymeric membrane by sequentially exposing the material to polyacrylic acid (PAA)/ polyethylene oxide (PEO)/ PAA/ polyvinylpyrrolidone (PVP)/PAA/PEO/(Ketjen Black, pH2). Each layer adheres based on hydrogen bonding. Deposition was performed by suspending the particle mass in 1 liter of deionized water with stirring and adding 1g of corresponding polymer as needed to build the layer by layer membrane. One rinse in 1-liter deionized water after each layer ensured the removal of excess, unabsorbed material. The product was then dried in the oven, under vacuum at 80 degrees Celsius as needed to dry, followed by EDS analysis to determine the selenium content.

Cathode powder preparation: The dry active material was ground with a pestle and mortar and mixed with the desired ratio 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.

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Cathode slurry preparation: A small ratio (1–10%) of a binder such as CMC/SBR 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.

Coin cell preparation: Disks with an area of 2.835 cm² 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 lithium disk (1.911 cm²) 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. No electrolyte leaks out in this procedure. The electrolyte used was a solution of 1 M LiTFSI, 0.02 M LiNO₃ in 1:1 DOL:DME. The cathode area is in excess in order to determine the minimum volume of electrolyte needed to extract full capacity. A typical open circuit potential of 2.8 V to 3.1 V is observed with an impedance below 100 Ω cm². Capacities are calculated based on the mass of selenium, sulfur or sulfur/selenium active material which corresponds to the limiting area of the lithium metal anode (1.911 cm²).

Supplementary Figures

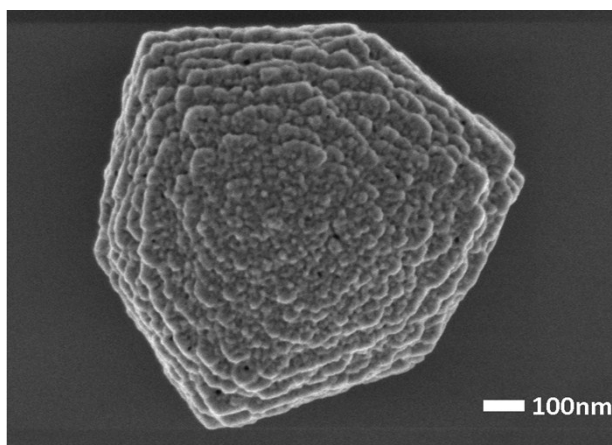


Figure S1. Rough, crystalline like selenium particle obtained when polyvinylpyrrolidone (PVP) is used as the templating agent.

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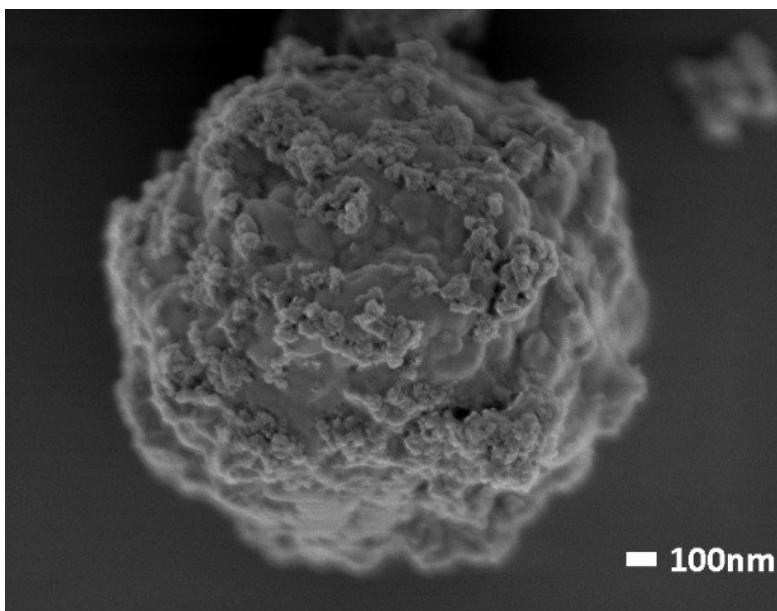


Figure S2. SEM Image of selenium active material particle wrapped in carbon containing polymeric protective membrane.

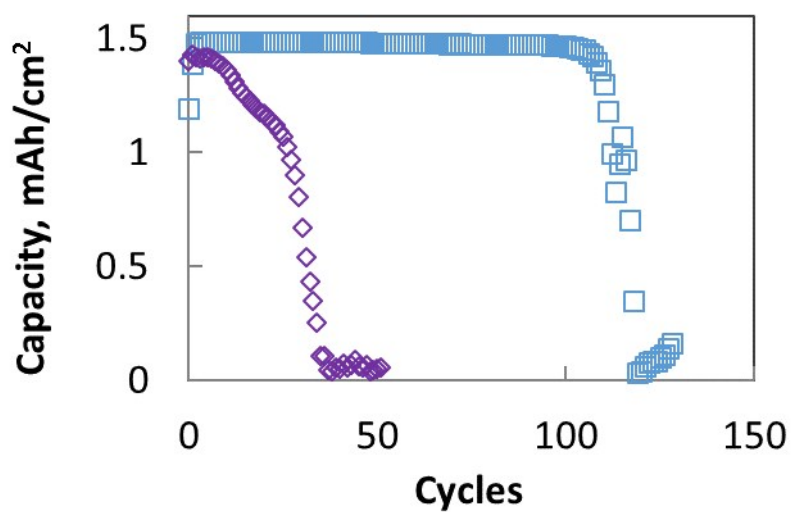


Figure S3. Stripping of deposited lithium from 1 M LiTFSI, 0.02 M LiNO₃/DOL:DME (blue squares) and 1 M LiPF₆/EC:DMC:DEC (purple diamonds) on a copper current collector with a lithium counter electrode in a 2032 coin cell with 210 μ l electrolyte and 1.55 mm fiber glass separator. 1.5 mAh/cm² lithium was deposited on each cycle followed by stripping (showed here). The deposition/dissolution rates were 2 mA/cm². All experiments were performed at room temperature.

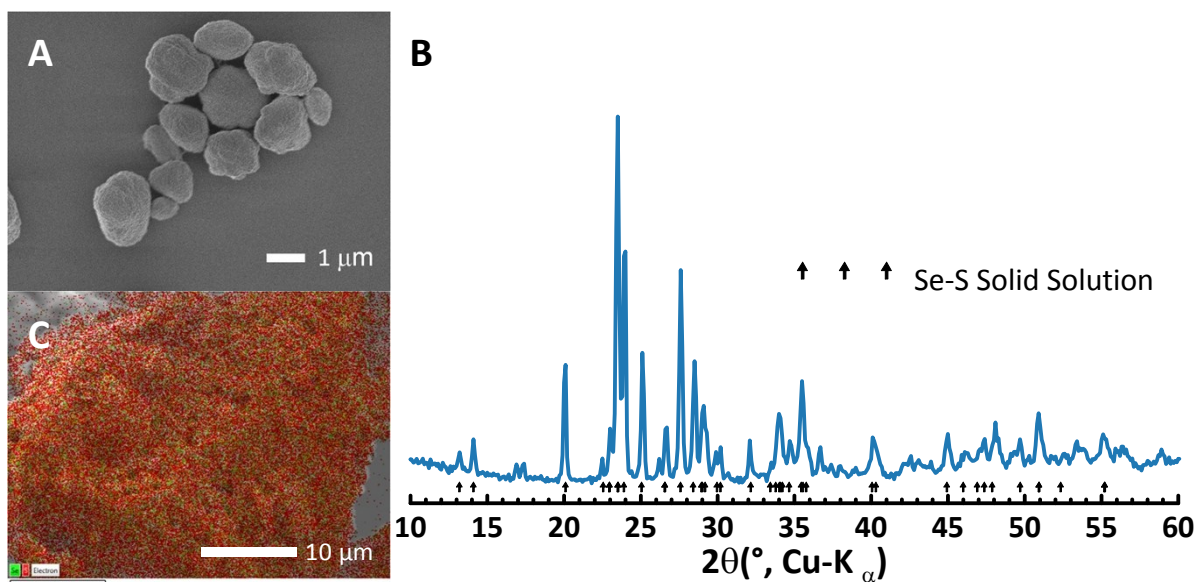


Figure S4. A) Sulfur/selenium hybrid particles without a protective polymeric membrane. B) XRD pattern of the hybrid particles, indexed to a sulfur/selenium solid solution¹ (ICSD: 1355). C) EDS map of the hybrid particles showing a homogeneous mixture of sulfur in red and selenium in green. The weight ratio of S:Se is 5:1.

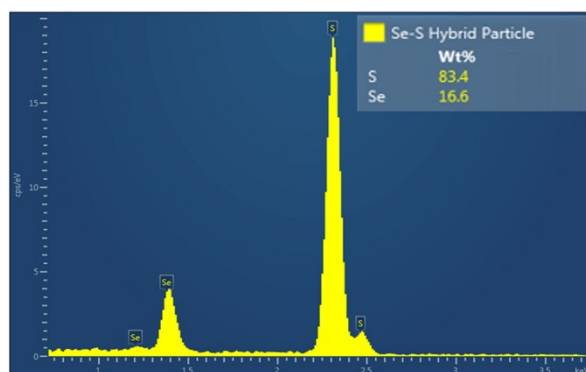


Figure S5. EDS of sulfur-selenium hybrid particle, revealing a S:Se weight ratio of 5:1.

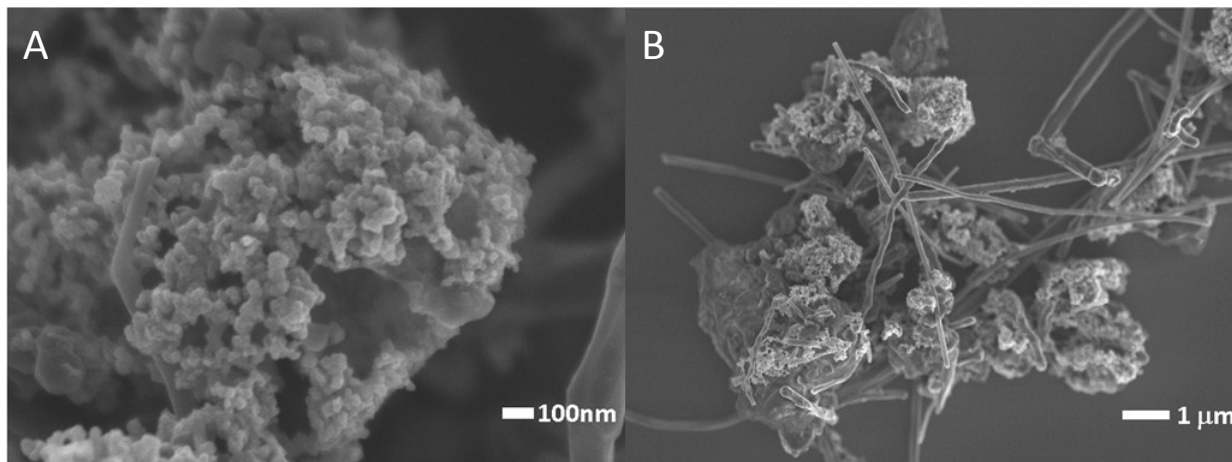


Figure S6. SEM images of A) the adhesion of carbon dots (Super P Li™) onto sulfur/selenium hybrids and B) the insertion of long-range carbon nanofiber electron pathways by low energy ball milling.

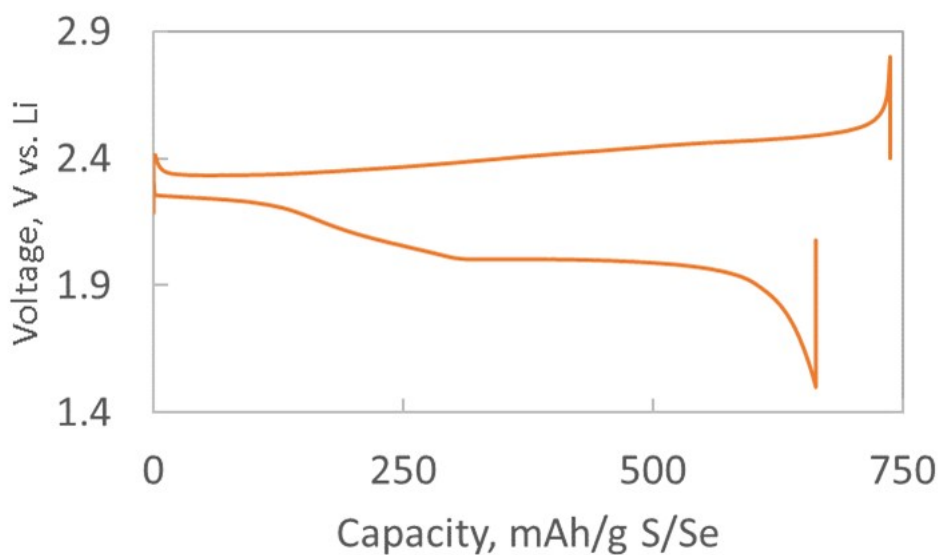


Figure S7. Discharge/charge curve of sulfur/selenium hybrid cathodes without a protective membrane in 1M LiTFSI, 0.02M LiNO₃, DOL:DME electrolyte.

Reference

1. Weiss, J. Mitteilung über interchalkogenverbindungen. IV. Röntgenographische untersuchungen an mischkristallen der zusammensetzung Se_nS_{8-n}. *Z. Für Anorg. Allg. Chem.* **1977**, 435 (1), 113–118 DOI: 10.1002/zaac.19774350115.