

Supporting Information

Optical and X-ray absorption interrogation of selenium-based redox in Li-S_xSe_y batteries

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Materials and methods

Chalcogen powders (S, Se) were purified via multi-chamber distillation, as reported by Boyd et al.¹ Vapor-deposition protocols were adapted from those previously used to incorporate sulphur into porous carbon scaffolds.^{2,3,4} Briefly, carbon nanofoam paper (CNFP) electrodes (“40/300” formulation, dictating precursor quantities)² were cut to size and then placed into a PTFE infiltration chamber. The chamber bottom has a well into which we placed ~1 g of the chalcogen powder to be infiltrated (i.e. sulphur, selenium, or a 60/40 atomic ratio blend of sulphur/selenium), with a 1.5 cm diameter, and ~100 μm thick CNFP substrate suspended on a stainless-steel mesh above (0.5 mm gap). After sealing in ambient atmosphere, this chamber was then placed into a small muffle furnace for vapor infiltration. Temperatures vary depending upon the infiltrating material: 175 °C for S, 225 °C for the SSe blend, and 260 °C for Se only. Infiltration times were also varied to achieve the desired loading of the samples. Chalcogenide mass loadings were determined by taking CNFP electrode mass before and after infiltration. The resulting areal loading of the electrodes were 3.5-4.5 mg/cm² for the S and SSe samples and 1.5-2 mg/cm² for the Se samples.

Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) (Zeiss Supra 55) were used to image and analyse chalcogen@CNFP samples. Cross sections were created for imaging by fast-fracturing samples soaked in liquid nitrogen with a fresh razor blade.

Galvanostatic cycling of 2032-coin cells was used to assess lithium storage capacity of the cathodes. In an Ar-filled glovebox, chalcogen@CNFP cathodes were covered with Entek “Gold” separator, 1.7 cm in diameter and 20 μm thick wetted with 80 μL of 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 0.2M LiNO₃ DOL:DME, and then a 1.6 cm diameter, 600 μm thick Li metal chip (MTI). The full stack thickness was ~720 μm Ether electrolyte was used to facilitate the highest energy sulfur reaction. The coin cells were sealed with a crimper and then cycled with constant current (Maccor) at various rates with respect to the chalcogen content.

The optical cell setup for these experiments is a modified version of the setup reported elsewhere.⁵ In these cells, two acrylic plates with embedded quartz windows (1" diameter) are used to sandwich the electrodes (cathode: chalcogen@CNFP adhered to a copper metal strip; anode: Li metal pressed onto a copper metal strip). These electrodes are laid side by side on one of the plates approximately 6 mm apart such that the active portion is directly over the quartz window. A Viton O-ring (1" OD) is centred on the active area, and the top plate is used to complete the stack. Nylon screws are used to tighten the assembly with sufficient force to compress the O-ring and make a liquid-tight seal. The electrolyte (1M LiTFSI and 0.2 M LiNO₃ in a 1:1 volume ratio of dioxolane:dimethoxyethane) is injected through the O-ring with a syringe. Cyclic voltammetry of these optical cells was performed using an Ametek PARSTAT MC Potentiostat with a PMC-1000 card at 0.1 mV s⁻¹ over a voltage range of 1.8–2.6 V.

Selenium K-edge XANES (X-ray absorption near-edge spectroscopy) spectra were collected (easyXAFS 300) on pouch cells containing a SSe@CNFP cathode (24 cm² and 28.6 mg chalcogenide loading) and a lithium metal counter/reference electrode. Prior to XANES measurements, cells were preconditioned voltammetrically (Gamry Ref 600) at 1 mV/s from 1.8–2.6 V for three cycles. For in situ XANES measurements, the cell voltage was swept at 1 mV/s between voltage points of interest and held potentiostatically during XANES acquisition. At each point of interest, the voltage was held for 30 minutes to allow the cell to reach a steady-state current before XANES spectra were collected. Metallic selenium was used as an energy calibration (12.68 keV). Three consecutive spectra (~30 minutes per scan) were collected and averaged for each voltage of interest.

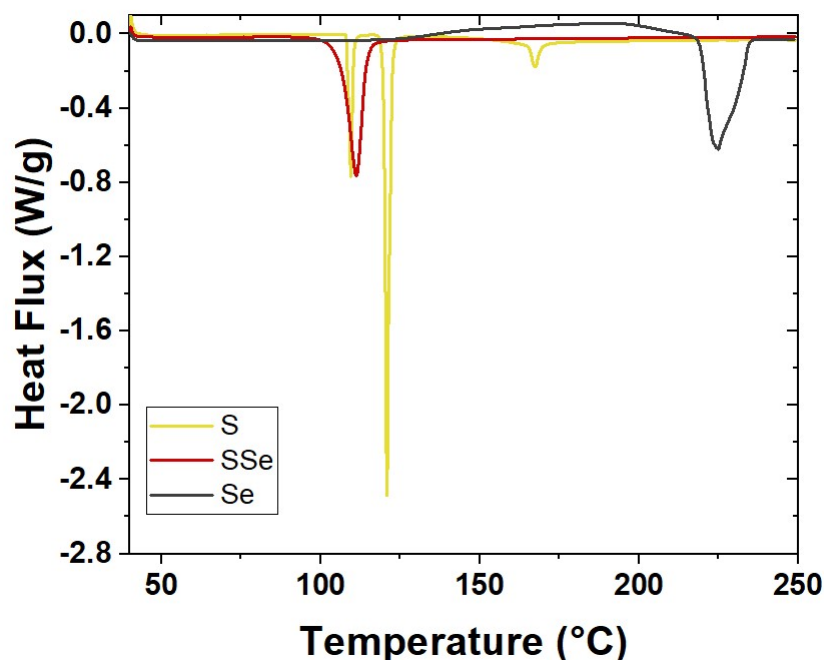


Fig. S1 Differential scanning calorimetry (DSC) of each precursor chalcogen or chalcogen blend.

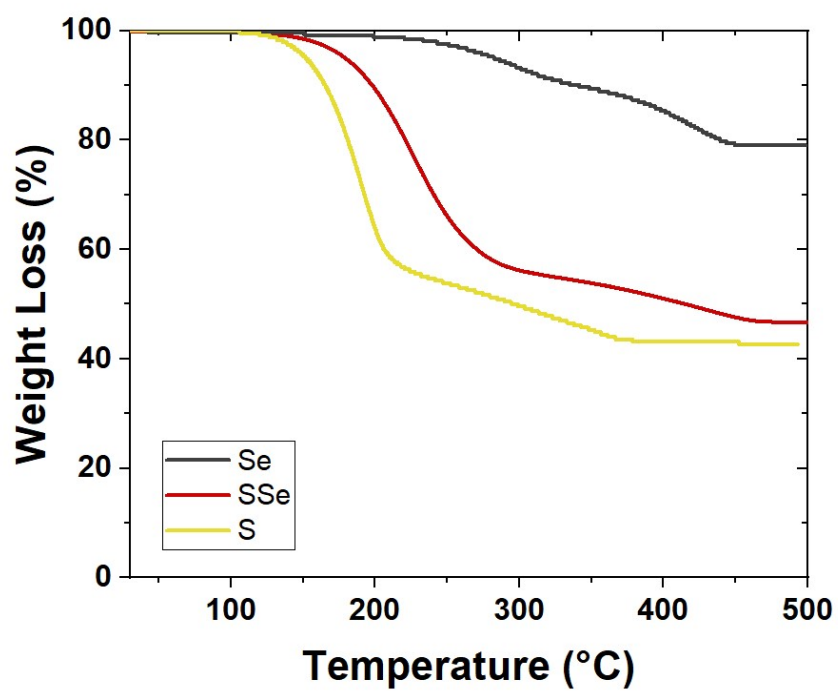


Fig. S2 Thermal gravimetric analysis (TGA) of each chalcogen@CNFP.

Table S1 Vapor loading conditions for each precursor and corresponding mass and volume loadings

Precursor	Vapor Exposure Temperature (°C)	Time (hr)	Mass Loading (%)	Volume Loading (%)
Sulfur (S)	175	4	50	32 (38% porous)
Sulfur-Selenium (SSe)	225	4	50	14 (56 % porous)
Selenium (Se)	260	4	31	6 (64 %porous)

Table S2: Comparison of chalcogen@CNFP mass loadings

Sample	Mass before infiltration (mg)	Mass after infiltration (mg)	Chalcogen loading (wt%)	Chalcogen loading from TGA (wt%)
S	2.32	4.37	53	57
SSe	2.02	4.20	48	53
Se	2.2	2.60	18	21

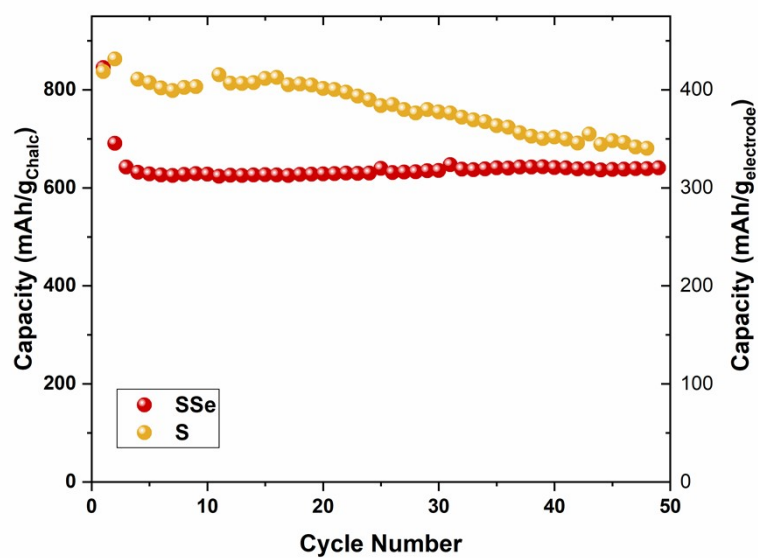


Fig. S3 Long-term, galvanostatic cycling of Li-S@CNFP and Li-SSe@CNFP cells at 0.1 A g⁻¹.

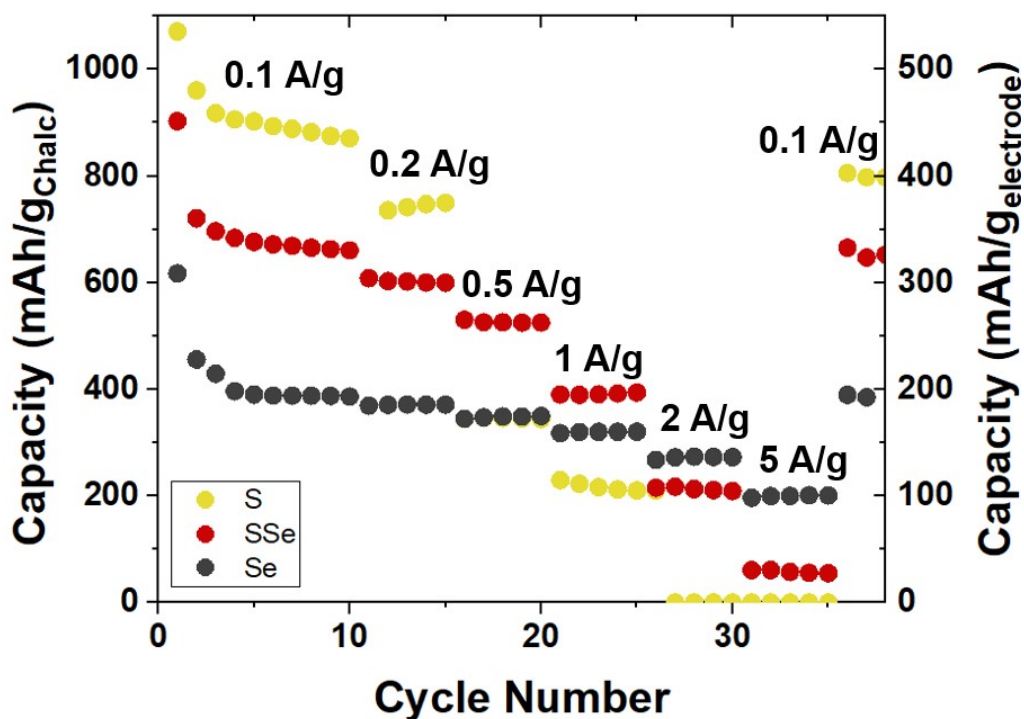


Fig. S4 Waterfall plot of discharge capacity for chalcogen@CNFP electrodes. Current density normalized to chalcogen mass.

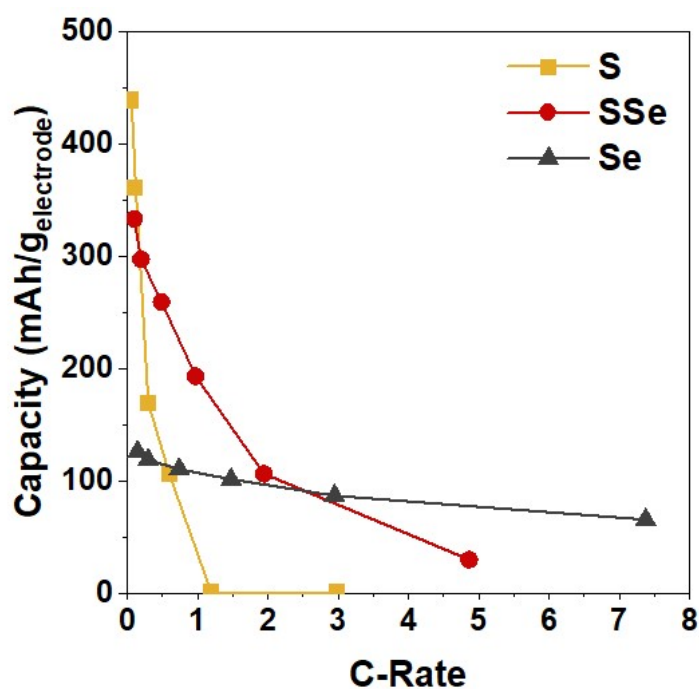


Fig. S5 Discharge capacity of chalcogen@CNFP electrodes normalized to the entire cathode mass as a function of C-rate.

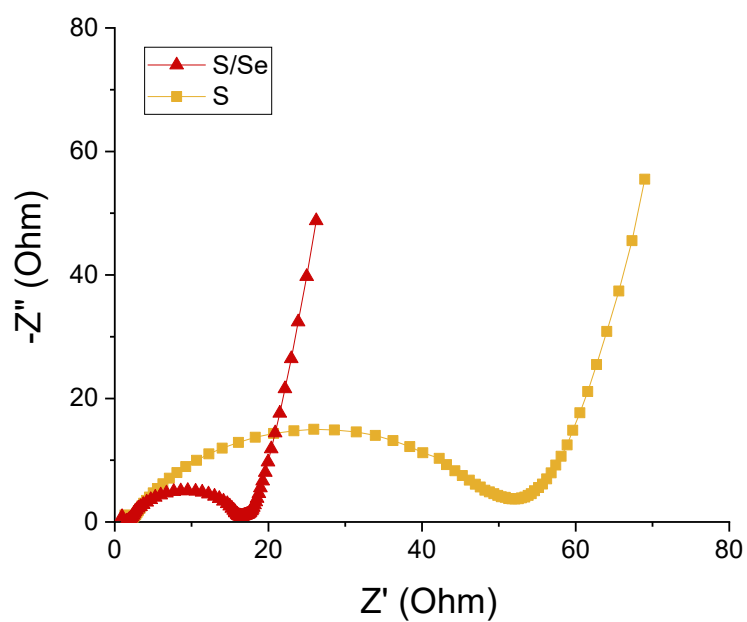


Fig. S6 Nyquist plot from electrochemical impedance spectroscopy of Li-S@CNFP and Li-SSe@CNFP cells.

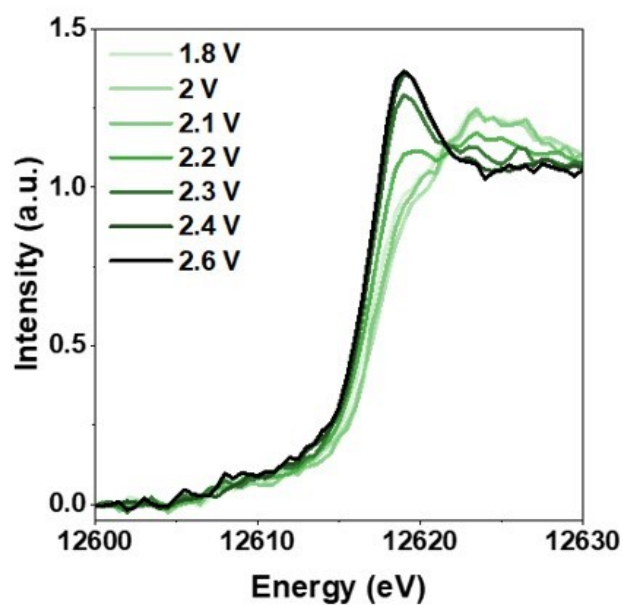


Fig. S7 in situ XANES spectra at selected cell voltages during charge of a Li-SSe@CNFP cell.

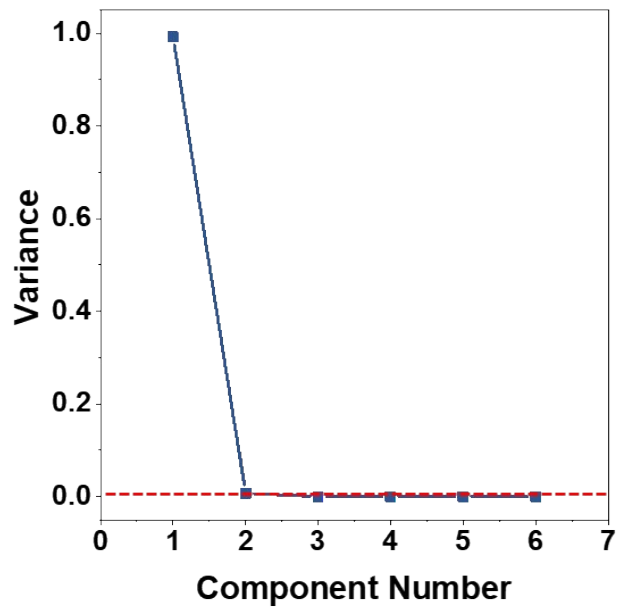


Fig. S8 Principal component analysis (PCA) scree plot derived from the in situ XANES spectra at selected cell voltages during discharge of a Li-S₂Se@CNFP cell.

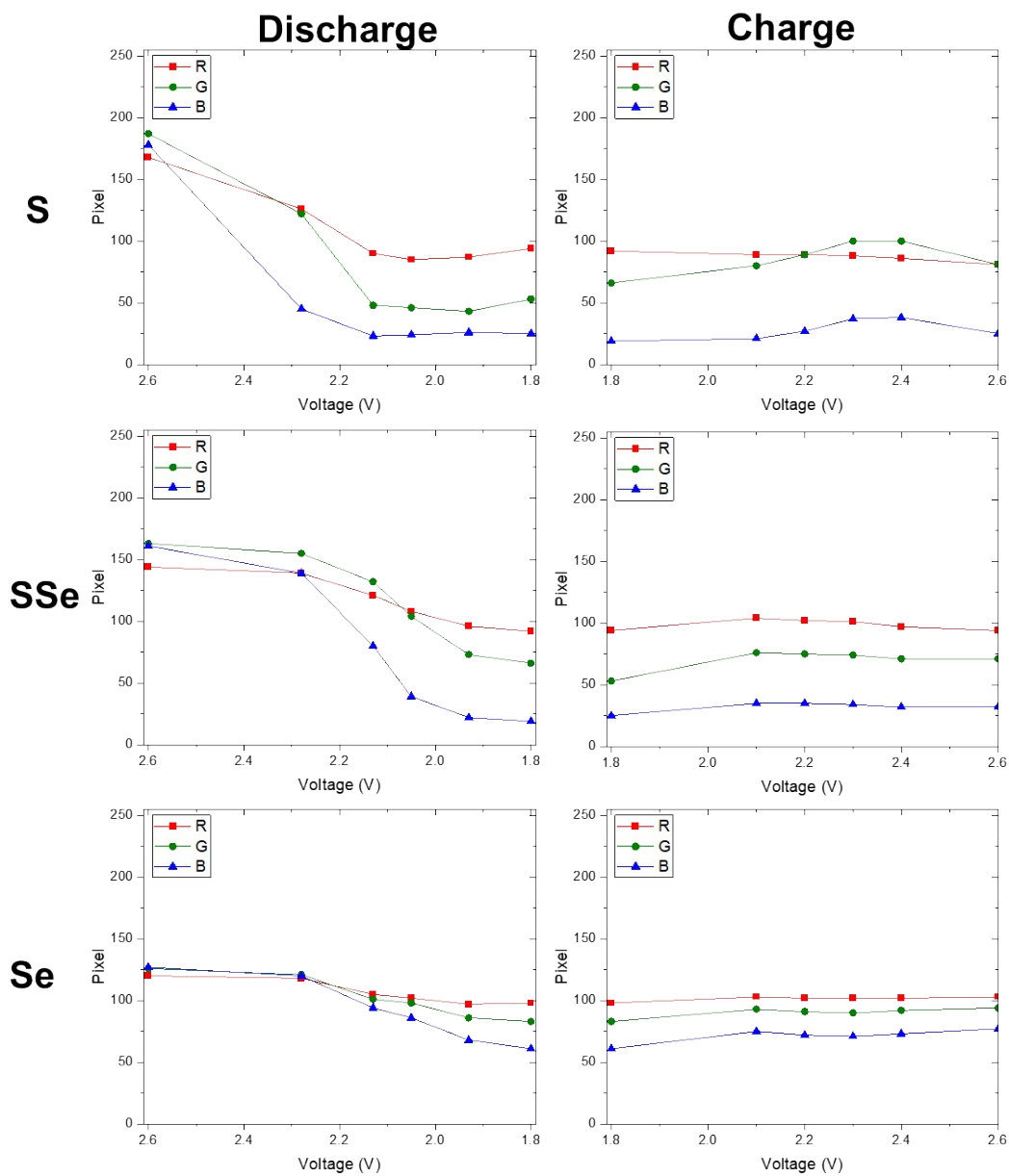


Fig. S9 Average RGB values of the electrolyte as a function of potential.

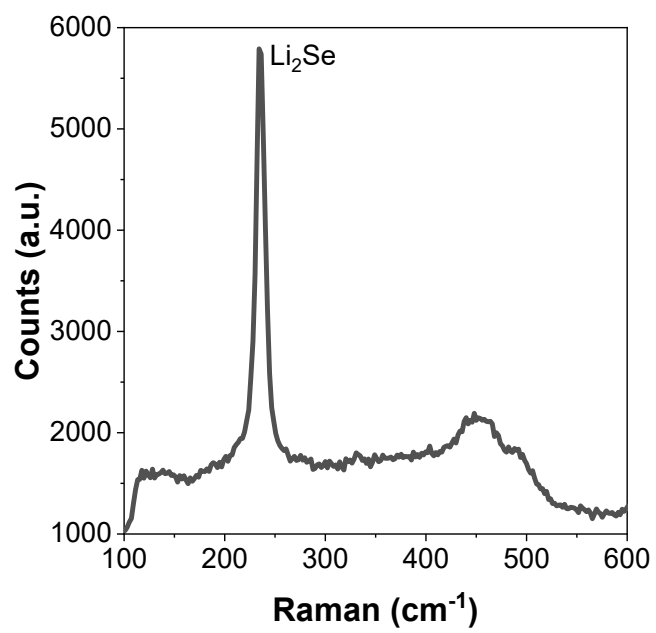


Fig. S10 Raman spectrum of discharged Li-SSe@CNFP cathode with Li₂Se peak at ~220 cm⁻¹.

References

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