SUPPLEMENTARY INFORMATION

Implications of in-situ chalcogen substitutions in polysulfides for rechargeable batteries

Sanjay Nanda\textsuperscript{a}, Amruth Bhargav\textsuperscript{a}, Zhou Jiang\textsuperscript{a}, Xunhua Zhao\textsuperscript{a}, Yuanyue Liu\textsuperscript{a}, and Arumugam Manthiram\textsuperscript{*a}

\textsuperscript{a}Materials Science and Engineering Program and Texas Materials Institute, The University of Texas at Austin, Austin, TX78712, USA

*Corresponding author: Tel: +1-512-471-1791; fax: +1-512-471-7681.
E-mail address: manth@austin.utexas.edu (A. Manthiram)

Figure S1. Mass spectra obtained with LC-MS for the [Li$_2$S$_6$ + Se] and [Li$_2$S$_6$ + Te] solutions, indicating the formation of a range of dianions and radical anions: SeS$_5^{2-}$, SeS$_3^{2-}$, TeS$_5^{2-}$ and TeS$_2^{-}$, which are confirmed by the distinct isotopic signatures of Se and Te. The insets show the relative intensities of the peaks predicted by theory.
**Figure S2.** S 2p spectra for [Li$_2$S$_6$ + Se] and [Li$_2$S$_6$ + Te] show the bridging and terminal sulfur atoms in the polyselenosulfide and polytellurosulfide chains. Quantification of the S 2p spectra with corresponding Se 3d and Te 3d spectra reveal that the Se : S ratio is 0.07 and the Te : S ratio is 0.025 (a complete dissolution of Se and Te in the 0.1 M Li$_2$S$_6$ + 0.06 M Se/Te would imply a ratio of 0.1)
**Figure S3.** Bader charge analysis of Li$_2$TeS$_5$ and Li$_2$SeS$_5$ with negative and positive signs representing the charge loss and gain, respectively. The Te atoms are more positively charged than the Se atoms on account of the larger difference in Pauling electronegativity between Te and S (0.48) compared to that between Se and S (0.03).

**Figure S4.** Change in color of polypropylene separator from white to yellow due to polysulfides seeping in from the [Li$_2$S + 0.1 S] cathode and from white to brown due to polyselenosulfides seeping in from the [Li$_2$S + 0.1 Se] cathode. The separator shows no such color change with the [Li$_2$S + 0.1 Te] cathode.
**Figure S5.** Log of peak currents in mA ($i_p$) plotted against log of scan rate in mv/s ($v$) and fitted with a straight line to yield the kinetic descriptor $\beta$ from the slope. The value of $\beta$ increases from 0.52 to 0.64 with the introduction of Se, which indicates an improvement in redox kinetics.
Figure S6. Charge-discharge plots for the first 25 cycles for Li || Li₂S half cells with 0.1 S (polysulfide), 0.1 Se (polyselenosulfide), and 0.1 Te (polytellurosulfide) additives, indicating the improvement in cathode utilization and overpotentials with the addition of selenium. The low Coulombic efficiency with 0.1 Te additive in the first cycle can be explained by the side reaction of elemental tellurium with polysulfides to form polytellurosulfides, which appears as an abnormally high charge capacity.
**Figure S7.** Electrochemical impedance spectroscopy of Li || Li symmetric cells with electrolytes containing polysulfide, polyselenosulfide, and polytellurosulfide additives after 20 cycles of lithium plating and stripping at 2 mA cm$^{-2}$ and 2 mAh cm$^{-2}$. The charge-transfer resistance $R_{ct}$ decreases in the order polysulfides > polyselenosulfides > polytellurosulfides.

**Figure S8.** Overpotentials of lithium plating and stripping in Li || Li symmetric cells with electrolytes containing polysulfide, polyselenosulfide, and polytellurosulfide additives. The presence of polytellurosulfides enables the most stable overpotentials with cycling.
Figure S9. SEM images of deposited lithium in Li || Li symmetric cells with electrolytes containing polysulfide, polylselenosulfide, and polytellurosulfide additives. The presence of polytellurosulfides enables smooth, planar, and homogeneous deposition of lithium, in contrast to the high-surface area mossy growths observed with polysulfides and polyselenosulfides.

Figure S10. Capacity retention of an anode-free Ni || Li$_2$S full cell employing 0.05 Se + 0.05 Te additives, compared with just 0.1 Se and 0.1 Te additives. A synergetic effect is partially realized – initial discharge capacities are improved with 0.1 Te and cycling stability is improved with 0.1 Se. However, it is speculated that the instability of polyselenosulfides (SeS$_2$•- radical) precludes an improvement in cycle life that is comparable to that with 0.1 Te.
Figure S11. Electrochemical performances of anode-free Ni || Li$_2$S pouch full cells with 10 wt. % tellurium (Te : Li$_2$S molar ratio = 0.04) or 10 wt. % carbon black as cathode additives for nearly 300 cycles. The N/P ratio is equal to 1, the E/Li$_2$S ratio is 4.5 µl mg$^{-1}$, the Li$_2$S loading is 4.2 mg cm$^{-2}$, and the C-rate is C/10. The absence of a steep drop off in capacity indicates that the electrolyte does not dry out.

Figure S12. S 2p, Li 1s, and C 1s spectra for the lithium surface in anode-free Ni || [Li$_2$S + 0.1 S] full cell. The S 2p spectra is dominated by oxidized sulfur species from electrolyte decomposition, which is validated by the prominent peak for CF$_3$ groups in the C 1s spectra. The Li 1s spectra helps deconvolute the Se 3d spectra for the lithium surface in the cell with 0.1 Se additive.
Figure S13. Comparing the depth profiles for SeS⁻, SeO⁻, TeS⁻, and TeO⁻, showing that selenium and tellurium atoms on the lithium surface are primarily bonded with oxygen and sulfur, respectively.

Figure S14. Normalized depth profiles for LiSe⁻ and LiTe⁻ reveal that fully reduced species such as Li₂Se and Li₂Te are present throughout the depth of the deposited lithium.
Figure S15. (a) Possible paths for Li$^+$-ion migration in Li$_2$TeS$_3$. One path (like 2-6) represents part of a complete pathway (like 2-6-3). (b) The chart shows barrier energies for all possible paths between adjacent Li atom sites based on single-ion migration.