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## Mixture is Better: Enhanced Electrochemical Performance of Phenyl Selenosulfide in Rechargeable Lithium Batteries

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Phenyl selenosulfide (PhS-SePh) is synthesized by an exchange reaction between phenyl disulfide and diselenide. PhS-SePh possesses average values of lattice parameter, bond character, and the lowest unoccupied molecular orbital as expected, but displays higher discharge voltage plateau and much better cycling stability than the two precursors in rechargeable lithium batteries.

Electrical energy storage has become unprecedentedly important for advanced portable electronics and electric vehicles. Lithium-ion (Li-ion) batteries have the highest specific energy and energy density among rechargeable battery systems, depending on the ion intercalation mechanism which has the advantages of high reversibility and high voltage in transition metal oxides such as LiCoO<sub>2</sub>.<sup>1</sup> Driven by the demand of high energy batteries, alternative cathode materials such as sulfur and oxygen with high specific capacities have been actively pursued in recent years.<sup>2-5</sup> The ion storage mechanism relies on the conversion reactions, e.g., sulfur to lithium sulfide, which typically involve frequent bond breaking and formation resulting in huge volume increases, dramatic structural transitions, and phase changes.<sup>6</sup> These complicated conversion processes result in the instability of cycling performance, therefore rendering them unsuitable for practical applications. utilize the high capacities of these materials, our То understanding in chemical bonds and their behavior in lithium batteries needs to be advanced. Therefore, new approaches could be developed to tackle the intrinsic issues preventing their widespread application.

Elemental sulfur has a theoretical specific capacity of 1675 mAh  $g^{-1}$  and forms a crystal structure composed of octa-atom

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ring at room temperature. The sulfur-sulfur (S-S) bonds break to form lithium polysulfide  $Li_2S_x$  (x = 2-8) when electrochemically reduced in lithium batteries.<sup>2</sup> However, sulfur and its reduced compounds are not conductive, therefore a significant amount of carbon in the electrode is needed. Recently, selenium as an electrode material in lithium and sodium batteries has attracted a lot of attention because of its higher electrical conductivity (10<sup>-5</sup> S cm<sup>-1</sup>) and mass density (4.82 g cm<sup>-3</sup>).<sup>7-15</sup> But elemental selenium has a low theoretical specific capacity of 675 mAh g<sup>-1</sup> due to its large molecular weight. Inorganic S-Se mixture compounds such as  $\mathsf{S}_x\mathsf{Se}_y$  with various atomic ratios have shown interesting properties and performance in rechargeable lithium and sodium batteries,<sup>7,16-21</sup> for example their specific capacities are higher than that of selenium and their conductivity is better than that of sulfur. S<sub>x</sub>Se<sub>y</sub> undergoes an intertwined reduction process forming discharge products of Li<sub>2</sub>S and Li<sub>2</sub>Se, resulting in a complicated conversion reaction. In addition, S<sub>x</sub>Se<sub>y</sub> has a disordered structure and the bond breaking and formation in S<sub>x</sub>Se<sub>y</sub> are random,<sup>22</sup> which add complexity in understanding the S-Se bonds in batteries. Recently, organopolysulfides have been studied as cathode materials in lithium batteries and shown unique properties such as ease of synthesis, structural tunability, and precise active sites.<sup>23-25</sup> They were also used as additives in electrolyte or solid-electrolyte interphase.26,27 These merits make them useful for studying S-S, and potential Se-Se and S-Se bonds in lithium and other battery systems.

Herein, we select phenyl selenosulfide (PhS-SePh), an organic compound containing a single S-Se bond to understand its property and electrochemical behavior in rechargeable lithium batteries. Phenyl disulfide (PhS-SPh) and diselenide (PhSe-SePh) were selected as precursors and control compounds. They could undergo an exchange reaction to form PhS-SePh, as shown in Figure 1a.<sup>23</sup> PhS-SePh can also be synthesized by chloramination reactions with mixtures of thiols and selenols, which involve multiple steps of synthesis and purification.<sup>28</sup> Our calculation shows the energy change for the exchange reaction is slightly negative, which is consistent with data in literature,<sup>22</sup> indicating a spontaneous reaction. The theoretical specific capacity of PhS-SePh falls in between those of PhS-SPh and PhSe-SePh when 2e<sup>-</sup> transfer is considered for all three compounds. The reaction is straightforward, where equimolar PhS-SPh and PhSe-SePh were

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mixed in dimethoxyethane and stirred for 30 min. PhS-SePh was formed once the solvent was removed. The scanning



Figure 1 (a) Scheme of reaction of phenyl disulfide (PhS-SPh) and phenyl diselenide (PhSe-SePh) to form phenyl selenosulfide (PhS-SePh) along with their specific capacities. (b) View of the unit cell of PhS-SePh along c axis. (c) X-ray diffraction patterns of three compounds. (d) Mass spectrum of the synthesized PhS-SePh.

electron microscopy (SEM) image and elemental mappings are shown in Figure S1, which shows that the sulfur and selenium atomic ratios are almost the same in the prepared sample. Based on our calculation, the crystal structure of PhS-SePh is the same as those of PhS-SPh and PhSe-SePh except lattice parameters are the average values. For example, the calculated c value is 23.125 Å, whereas the c values of PhS-SPh and PhSe-SePh are 22.924 Å and 23.450 Å,<sup>29</sup> respectively, as shown in Table S1. The view along the a axis of the crystal structure of PhS-SePh is shown in Figure 1b. Sulfur and selenium moieties form one-dimensional lines which are separated by phenyl rings. S-Se moieties are close in pair, but far from others in the structure.

X-ray diffraction (XRD) was used to confirm the crystal structure of the synthesized PhS-SePh. The full XRD patterns are shown in Figure S2, which resemble the calculated ones in Figure S3. Figure 1c shows XRD patterns in the 20 ranges of 11-12° and 21-24° where distinct separations are observed. It can be seen that PhS-SPh and PhSe-SePh show a single peak of (011) plane at 11.5° and 11.3°, respectively, PhS-SePh also shows a single peak of (011) plane at 11.4°. In addition, all compounds show a set of four peaks of (020), (021), (006), and (022) planes in the 21-24° region. All the peaks of PhS-SePh fall in between those of PhS-SPh and PhSe-SePh. The XRD results indicate the synthesized PhS-SePh compound is quite pure since no other impurity or overlapped peaks are observed. In addition, the crystal structure of PhS-SePh is the same as those of PhS-SPh and PhSe-SePh, which confirms the accuracy of the predicted crystal structure shown in Figure 1b. This proposed crystal structure is further validated through Fourier transform infrared (FTIR) spectroscopy shown in Figure S4. When looking at the 440-485 cm<sup>-1</sup> region, the out of plane phenyl ring twist occurring at 456 cm<sup>-1</sup> for PhS-SePh is in between that of PhS-SPh (463 cm<sup>-1</sup>) and PhSe-SePh (455 cm<sup>-1</sup>). Furthermore, the transition of symmetric S-S stretch from 472.6 cm<sup>-1</sup> in PhS-SPh to the asymmetric stretch of the S-Se bond in PhS-SePh leading to a doublet at 471.6 cm<sup>-1</sup> and 477 cm<sup>-1</sup> can be observed.<sup>30</sup>

To further confirm the success of forming PhS-SePh via this synthesis route, gas chromatography-mass spectrometry (GC-MS) were performed. Figure S5 presents the GC spectrum of PhS-SePh. Three peaks at retention times of 14.1, 14.6, and 15.1

min are seen. The peak at 14.6 min is attributed to PhS-SePh. The corresponding mass spectrum is shownin Figure 1d407be parent ion peak at m/z of 266.0 corresponds to the molar mass of PhS-SePh. Other daughter fragmentation peaks corresponding to that of PhS-Se (phenyl sulfoselenide radical, m/z = 186.0), PhSe· (phenyl selenide radical, m/z = 157.0), ·S-Se· (sulfoselenide radical, m/z = 109.0) and PhS· (phenyl sulfide radical, m/z = 77.1) are also evident. The peaks at 14.1 and 15.1 min can be assigned to PhS-SPh and PhSe-SePh, respectively, based on the m/z ratios in Figure S6. The presence of two precursors is believed to be due to the heating injection process which causes disproportionation of PhS-SePh into PhS-SPh and PhSe-SePh. We also performed nuclear magnetic resonance (NMR). Figure S7 shows the <sup>13</sup>C-NMR spectra of these compounds, which also supports the success of making PhS-SePh via this route.

To understand the S-Se bond nature in PhS-SePh in catholyte solution, we calculate the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), and bond energies using an implicit solvation model. Figure 2a shows the LUMO/HOMO energy levels of the three compounds. The LUMO are in the order of PhSe-SePh (-0.99 eV) < PhS-SePh (-0.86 eV) < PhS-SPh (-0.69 eV). For molecules with similar structures, LUMO levels correlate with the reduction potential in batteries, and a lower LUMO energy corresponds to a higher reduction potential.<sup>31</sup> It is thus expected that the discharge voltage plateau of these compounds would follow the reverse order. Figure 2b shows the bond energies of the three compounds. The S-S bond has a higher bond energy than that of the Se-Se bond because of the higher electronegativity and smaller ionic radius of sulfur compared to selenium. The S-Se bond energy stays in the middle of the S-S and Se-Se bond energies as expected. The energy changes of lithiation reactions of PhS-SPh, PhSe-SePh, and PhS-SePh are shown in Table S2.

To evaluate the electrochemical behavior of these compounds, 0.5 M catholytes were prepared and tested in bulky paper current collector which has been successfully used in our previous studies.<sup>31</sup> Figure 3a shows the cyclic voltammogram (CV) of three cells with PhS-SPh, PhSe-SePh, and PhS-SePh catholytes. All of them show single cathodic and anodic peaks. PhSe-SePh shows fast kinetics (i.e., small peak separation) compared to PhS-SPh and PhS-SePh due to the low Se-Se bond energy. The onset cathodic potentials are in the order of PhS-SPh < PhSe-SePh < PhS-SePh and the onset anodic potentials are in the order of PhSe-SePh = PhS-SePh < PhS-SPh. Figure 3b shows the voltage profiles of these cells, which exhibit single discharge and charge voltage plateaus. The discharge voltage plateaus are in the order of PhS-SPh (2.1 V) < PhSe-SePh (2.2 V) < PhS-SePh (2.22 V). It is interesting that the



Figure 2 (a) Lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of PhS-SPh. PhSe-SePh. and PhS-SePh. (b) Sulfur-sulfur (S-S), selenium-selenium (Se-Se), and sulfur-selenium (S-Se) bond energies in these compounds.

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Figure 3 (a) Cyclic voltammogram, (b) voltage profiles, and (c) cycling performance of 0.5 M PhS-SPh, PhSe-SePh, and PhS-SePh catholytes, the cells were cycled at C/5. (d) Cycling performance of 1.0 M catholytes of these compounds at C/5.

discharge voltage plateau of PhS-SePh is slightly higher than that of PhSe-SePh, which is consistent with the CV result in Figure 3a but inconsistent with the calculated LUMO levels shown in Figure 2a. We postulate that this anomaly can be explained through thermodynamics. It is known that the reaction voltage can be determined from the difference in the Gibbs free energy ( $\Delta G = \Delta H - T\Delta S$ ) between the reactant and the product. Given that the energy between S-Se bond is very close to that of pure S-S and Se-Se bonds, it is reasonable to expect little to no change in the enthalpy term. However, the mixing of the discharged products, PhSe-Li and PhS-Li could result in the relatively larger entropy term in the case of PhS-SePh which would be absent in the case of PhSe-SePh and PhS-SPh since only a single product, either PhSe-Li or PhS-Li, is formed. The resultant lowering of Gibbs free energy for the reaction products leads to higher reaction voltage observed in PhS-SePh. The charge voltage plateaus are in the order of PhSe-SePh < PhS-SePh < PhS-SPh. PhS-SPh shows the highest voltage hysteresis which has been observed in prior literature, <sup>32,33</sup> while PhSe-SePh shows the lowest, which is related to the bond energy resulting in different overpotential.

Figure 3c shows the cycling performance. The initial capacities are in the order of PhSe-SePh (141 mAh g<sup>-1</sup>) < PhS-SePh (152 mAh  $g^{-1}$ ) < PhS-SPh (185 mAh  $g^{-1}$ ), which are consistent with their theoretical values. However, the capacities of PhS-SPh and PhSe-SePh degrade very fast and fall below 50 mAh g<sup>-1</sup> after 100 cycles, which is due to the solubility of PhSLi and PhSeLi in the electrolyte that leads to the loss of active material and consequently shorter cycle life. In contrast, PhS-SePh shows a much better cycling performance with a capacity retention of 52% (79 mAh g<sup>-1</sup>) over 200 cycles. The cell also shows good rate performance (Figure S8). To exclude the effect of catholyte concentration, 1.0 M catholytes were also evaluated. Figure S9 shows the voltage profiles of the three compounds, clearly PhS-SePh has the highest discharge voltage plateau. More interestingly, PhS-SePh shows the highest initial discharge capacity which is partially due to the incomplete discharge of PhS-SPh because of the high ohmic overpotential. Figure 3d shows the cycling performance. Again, the discharge capacity of PhS-SPh degrades very fast. However, PhSe-SePh shows better cycling

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Figure 4 (a) SEM images of (a) PhS-SPh, (b) PhSe-SePh, and (c) PhS-SePh electrodes after discharge, the scale bar is 1  $\mu$ m. (d) Nyquist plots of these cells, the PhS-SPh plot fits to the equivalent circuit model shown in the figure.

stability than the 0.5 M PhSe-SePh catholyte but high capacity fade persists. In contrast, PhS-SePh shows the highest capacity and best cycling stability over 200 cycles. Selected voltage profiles are presented in Figure S10. In addition, the Coulombic efficiencies of the two cells with PhS-SePh catholytes are >99.5%, representing high reversibility. The battery performance results prove the mixture PhS-SePh is the best cathode material among three compounds in rechargeable lithium batteries. Additionally, the density of PhS-SePh is 1.597 g cm<sup>-3</sup>, which is between that of PhS-SPh (1.353 g cm<sup>-3</sup>) and PhSe-SePh (1.84 g cm<sup>-3</sup>). Based on the performance shown above, the specific energy is estimated to be 337 Wh kg<sup>-1</sup> and the energy density is 538 Wh L<sup>-1</sup>.

Figures 4 a-c show the SEM images of the three electrodes after discharge. PhS-SPh and PhSe-SePh electrodes look similar, in which agglomeration is seen and some carbon fibers are bare. In contrast, the PhS-SePh electrode is guite porous, in which all carbon fibers are coated with the discharged products. The observed morphology of the discharged electrodes supports the entropy effect claimed above. Due to the mixing process of PhS-Li and PhSe-Li being kinetically slower, uniform growth is observed. However, growth of the single solid phase of either PhSe-Li or PhS-Li is much faster and thus results in their agglomeration. Furthermore, this agglomeration of nonconductive PhS-Li results in the highest voltage hysteresis. In contrast, PhSe-Li shows much lower voltage hysteresis even though it agglomerates, which is believed to be due to the conductivity of Se. The mixture of PhS-Li and PhSe-Li is in good contact with conductive carbon nanofibers, therefore the voltage hysteresis is low. In addition to voltage hysteresis, this phenomenon can also explain the better longevity of PhS-SePh cells. The better adhesion of the mixed discharge products to the carbon substrate and the need to form S-Se bonds on charge minimizes the detachment and also dissolution of these particles leading to reduced shuttle effect and thus prolonged cycle life.

This phenomenon was further explored through electrochemical impedance spectroscopy (EIS). Figure 4d shows Nyquist plots of these cells after discharge. The intercepts in the real axis in the high frequency range are the bulk resistance and resistance of electrodes ( $R_{\Omega}$ ). The bulk resistance of liquid electrolyte can be considered to be the same in these cells. Therefore, the intercept difference is due to the resistance of electrodes which is in the order of PhSe-SePh (5 ohms) < PhS-

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SPh (29 ohms) < PhS-SePh (78 ohms). The high conductivity of selenium leads to the lowest resistance of the discharged electrode even though PhSe-Li agglomerates. Although the mixture of PhS-Li and PhSe-Li should be more conductive than PhS-Li, the coated carbon nanofibers in the case of PhS-SePh results in high resistance. More carbon exposure can be seen in the discharge electrode of PhS-SPh, which helps to maintain a lower resistance.

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All cells show a semi-circle in the high and medium frequency range, which can be represented as a single time constant of a double-layer capacitance (CPE<sub>dl</sub>) in parallel with a chargetransfer resistance (R<sub>ct</sub>), as shown in the equivalent circuit.<sup>34</sup> The diameter of the semi-circle is considered as  $R_{ct}$  between carbon fiber in the electrode and discharged product, which is in the order of PhS-SPh (188 ohms) < PhS-SePh (233 ohms) < PhSe-SePh (246 ohms). The R<sub>ct</sub> is the charge transfer barrier due to the difference in intimacy between the discharged products (PhS-Li, PhSe-Li, or PhSe-Li/PhSe-Li) and carbon current collector in the catholyte. PhS-Li seems to be most intimate with the carbon fiber, leading to low charge transfer resistance, whereas PhSe-Li is the least. This could be potentially due to the difference in the atomic size of sulfur and selenium or the affinity of the discharged products with carbon. In the lower frequency range, the PhS-SPh cell shows a linear plot which is due to the Warburg impedance (W). The other two cells show an incomplete semi-circle, which could be due to an additional time constant (not shown in the equivalent circuit). This study highlights the potential for additional characterization and simulation needed to further our understanding on the electrochemical behavior of these materials containing mixing chemical bonds.

In summary, we have successfully synthesized phenyl selenosulfide by an exchange reaction. PhS-SePh has the same crystal structure as those of PhS-SPh and PhSe-SePh, and it has an average specific capacity, cell parameter, and bond character. PhS-SePh shows an anomalously higher discharge voltage plateau than those of the two precursors and much better cycling stability. It is believed that the mixture has a higher entropy and lower thus Gibbs free energy, which also leads to much less agglomeration than the other two compounds in the discharged electrodes. The difference in the coating of the discharge products namely PhS-Li and PhSe-Li on carbon fibers in the current collector is also observed through EIS. This study reveals interesting electrochemical behavior of phenyl selenosulfide in rechargeable lithium batteries. The S-Se bond in organic compounds is a favorable active site for charge storage, its unique chemistry could be of interest to the chemistry and battery communities.

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## **Conflicts of Interest**

There are no conflicts to declare.

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