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Confined Lithium-Sulfur Reactions in Narrow-Diameter Carbon Nanotubes Reveal Enhanced Electrochemical Reactivity

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20 KEYWORDS: Lithium-sulfur battery, single-walled carbon nanotubes, sub-nano confined
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22 sulfur, electrochemical systems, controlled solid-state reactions
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28 ABSTRACT: We demonstrate an unusual electrochemical reaction of sulfur with lithium upon
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30 encapsulation in narrow-diameter (sub-nanometer) single-walled carbon nanotubes (SWNTs).
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32 Our study provides mechanistic insight on the synergistic effects of sulfur confinement and Li⁺
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34 ion solvation properties that culminate in a new mechanism of these sub-nanoscale-enabled
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36 reactions (which cannot be solely attributed to the lithiation-delithiation of conventional sulfur).
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38 Two types of SWNTs with distinct diameters, produced by electric arc (EA-SWNTs, average
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40 diameter 1.55 nm) or high-pressure carbon monoxide (HiPco-SWNTs, average diameter 1.0 nm),
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42 are investigated with two comparable electrolyte systems based on tetraethylene glycol dimethyl
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44 ether (TEGDME) and 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5). Electrochemical
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46 analyses indicate that a conventional solution-phase Li-S reaction occurs in EA-SWNTs, which
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48 can be attributed to the smaller solvated [Li(TEGDME)]⁺ and [Li(15-crown-5)]⁺ ions within the
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50 EA-SWNT diameter. In stark contrast, the Li-S confined in narrower diameter HiPco-SWNTs
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52 exhibits unusual electrochemical behavior which can be attributed to a solid-state reaction
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3 enabled by the smaller HiPco-SWNT diameter compared to the size of solvated Li^+ ions. Our
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5 results of the electrochemical analyses are corroborated and supported with various
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7 spectroscopic analyses including *operando* Raman, X-ray photoelectron spectroscopy, and first-
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9 principles calculations from density functional theory. Taken together, our findings demonstrate
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11 that controlled solid-state lithiation-delithiation of sulfur and an enhanced electrochemical
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13 reactivity can be achieved by sub-nano encapsulation and one-dimensional confinement in
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15 narrow-diameter SWNTs.
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24 Electrochemical reactions between lithium (Li) and sulfur (S) constitute the fundamental
25
26 building blocks for enabling rechargeable Li-S battery chemistries. When sulfur is in its native
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28 cyclo- S_8 molecular state and ethers are used as the electrolyte solvents, a series of complex
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30 lithiation reactions occur in the electrolyte, generating Li polysulfides that ultimately result in the
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32 precipitation of lower-order polysulfides or lithium sulfide. The exact chemical fate and transport
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34 processes in these uncontrolled interfacial chemical environments are poorly understood to date,
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36 which pose fundamental challenges to improving Li-S batteries. As an alternative strategy to
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38 controlling these chemical interactions, we have sought to shift the current Li-S electrochemical
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40 reaction paradigm from solution to the solid phase. Specifically, one of our previous studies
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42 suggested that the Li-S electrochemical mechanism is dictated by the geometry of the sulfur
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44 confinement,¹ and solid-state (or quasi-solid-state) Li-S electrochemical reactions could occur in
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46 liquid electrolytes by confining sulfur in sub-nanometer pores in microporous carbon. Due to the
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48 sub-nano pore size, solvated Li^+ ions enter the pores through a desolvation process so that solid-
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50 state or quasi-solid-state Li-S electrochemical reactions occur in this sub-nano confined
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3 environment. Similar solid-state Li-S electrochemical mechanisms enabled by sub-nanometer
4 confinement were also proposed by the Gentle² and Huang³ groups, with other hypotheses
5 including the existence of small sulfur allotropes in sub-nanometer confinements,⁴ carbon
6 sulfurization,⁵ and formation of solid electrolyte interphase (SEI) on the sub-nanometer confined
7 sulfur.^{6,7} In all of these previous studies, it is apparent that the physical confinement of sulfur
8 plays a crucial role in dictating the detailed electrochemical mechanisms in Li-S reactions.
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18 To further study the control over Li-S reactions in confined chemical environments, we utilize
19 single-walled carbon nanotubes (SWNTs) in this study to confine sulfur. SWNTs with
20 nanometer-sized diameters provide an ideal encapsulation host for sulfur because of their
21 intrinsic one-dimensional (1-D) confinement within the rigid but electronically-conductive
22 SWNT wall. Various materials including fullerenes,⁸⁻¹¹ inorganic molecules,¹²⁻¹⁶ organic
23 molecular dopants,¹⁷ metal and metal oxide catalytic nanoparticles^{18,19} have been encapsulated in
24 SWNTs. Recently in 2014, Fujimori *et al.* proposed that sulfur in a metallic state could be
25 confined in electric arc produced SWNTs (EA-SWNTs) with either linear or zigzag chain
26 structure.²⁰ Based on this proposed S@SWNT structure, Yang *et al.* studied the electrochemical
27 lithiation-delithiation of sulfur confined in EA-SWNTs,²¹ and their results demonstrated an
28 electrochemical behavior consistent with the typical solution-phase Li-S reaction.
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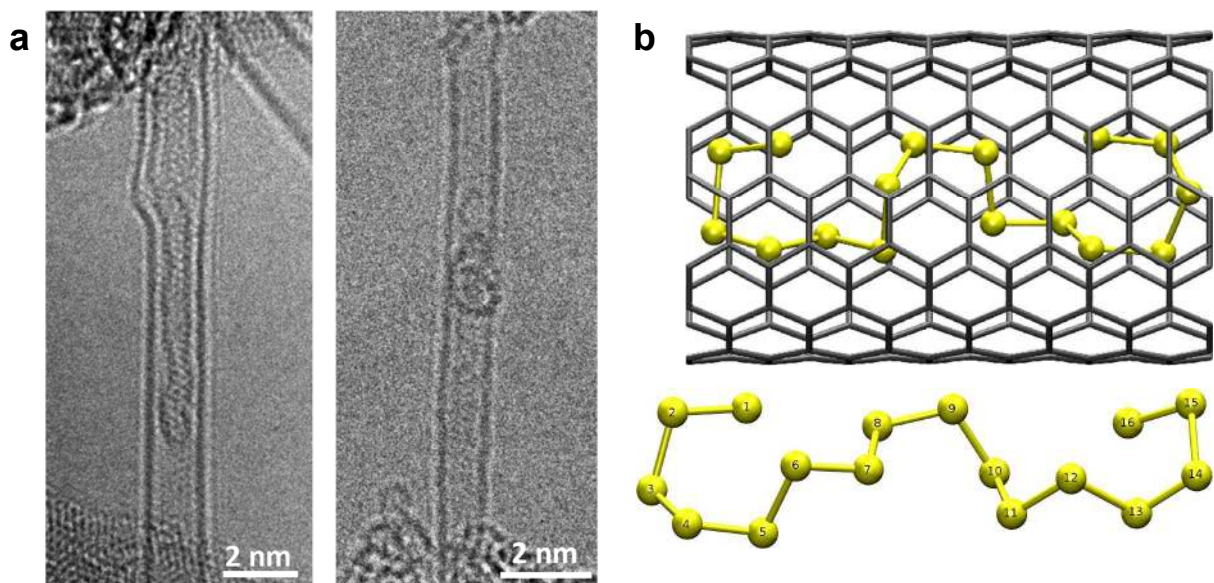
45 To demonstrate the effects of the confined chemical environment on Li-S reactions, we utilize
46 two types of SWNTs with different diameters, EA-SWNTs (average diameter = 1.55 ± 0.1 nm)
47 and high-pressure carbon monoxide produced SWNTs (HiPco-SWNTs, average diameter = $1.0 \pm$
48 0.2 nm), and two different electrolytes: 1 M lithium bis(trifluoromethane sulfonyl)imide
49 (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) and 1,4,7,10,13-
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3 pentaoxacyclopentadecane (15-crown-5), respectively. Structurally, 15-crown-5 molecule is the
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5 cyclo-counterpart of the linear TEGDME. The selection of these two solvents is based on the
6
7 rationale that the structures of solvated Li^+ ions in these two solvents differ solely due to the
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9 structures of the solvent molecules (linear vs. cyclic), thus providing a rigorous comparison of
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11 the Li-S electrochemical behavior in the EA-SWNTs and HiPco-SWNTs with distinct diameter
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13 sizes. Our findings are complemented by a suite of experimental and computational
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15 characterization techniques including *operando* Raman, X-ray photoelectron spectroscopy, and
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17 first-principles calculations from density functional theory.
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23 **Results/Discussion**

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26 Sulfur was infused into EA-SWNTs and HiPco-SWNTs *via* exposure to saturated sulfur vapor at
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28 600 °C for 2 days in sealed hourglass-shaped quartz tubes followed by the removal of superficial
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30 sulfur (exterior of the SWNTs), as detailed in the Methods/Experimental Section. According to
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32 our previous study, S_2 molecules generated at 600 °C can diffuse into the SWNTs and
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34 subsequently polymerize to form long-chain sulfur diradicals.²² The sulfur content was
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36 determined with elemental analysis *via* colorimetric titration (Figure S1 in Supporting
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38 Information): 4.57 wt.% in S@EA and 11.33 wt.% in S@HiPco. The sulfur contents were also
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40 confirmed by energy-dispersive X-ray spectroscopy analysis (EDX) and electron energy loss
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42 spectroscopy (EELS) (Figures S2 and S3 in Supporting Information). The microstructures of
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44 S@EA and S@HiPco were characterized with low-kV monochromated and aberration-corrected
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46 high-resolution transmission electron microscopy (HRTEM). As shown in **Figure 1a**, an
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48 irregularly-shaped sulfur chain can be observed to be folded inside an EA-SWNT with diameter
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50 of 1.5 nm; Similarly, a shorter swirl-like sulfur chain can be observed inside a HiPco-SWNT. It
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3 is worth mentioning that despite the low electron beam energy, the S@SWNTs was unstable
4 under prolonged beam irradiation: As shown in Figure S4 in Supporting Information, a breach on
5 the HiPco-SWNT wall in Figure 1a was quickly created by the electron beam, and the sulfur
6 chain escaped. Nevertheless, we observe the sulfur chains confined in the EA- and HiPco-
7 SWNTs do not have a well-defined structure and are distinctly different from the linear or zig-
8 zag structures previously proposed. Indeed, our density functional theory (DFT) based
9 calculations demonstrate that a more disordered structure of the sulfur chain is more stable than
10 the linear and zigzag conformations when they are confined in a SWNT.²² In particular, our DFT
11 optimizations depicted in **Figure 1b** show that the sulfur chain inside the SWNT tends to
12 accommodate conformations that resemble the cyclo-S₈ allotrope, *i.e.*, the bond distances, bond
13 angles, and dihedral angles are similar to the cyclo-S₈ allotrope geometry (see Table S1-4 in the
14 Supporting Information for further details and geometric analyses). Our optimized sulfur
15 geometries can be rationalized by recognizing that this allotrope is the most thermodynamically
16 stable form at ambient temperatures.²³



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3 **Figure 1.** TEM images of (a) S@EA (left) and S@HiPco (right); (b) Optimized geometry of a
4 sulfur chain inside a (7,7) SWNT (top) and view of the sulfur chain without the (7,7) SWNT
5 (bottom). The diameter of the optimized S@(7,7)SWNT is 9.93 Å. The optimized total electronic
6 energy is -1.6 KeV, and the cohesive energy is -0.9 eV.
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10 The primary Li^+ ion solvation structures in the electrolytes were characterized with electrospray
11 ionization mass spectrometry (ESI-MS). As shown in **Figure 2**, the exceptionally clean ESI-MS
12 spectra of 1 M LiTFSI in TEGDME and 15-crown-5 indicate that the exclusive solvated Li^+ ion
13 species are $[\text{Li}(\text{TEGDME})]^+$ ($m/z = 229.14$) and $[\text{Li}(15\text{-crown-5})]^+$ ($m/z = 227.12$), respectively.
14
15 The small peaks in the spectra ($m/z = 245.12$ and $m/z = 243.10$, respectively) can be attributed to
16 the small amount of impurities with one -OH group instead of H in the solvent molecules. The
17 insets of Figure 2 show the optimized solvation structures of $[\text{Li}(\text{TEGDME})]^+$ and $[\text{Li}(15\text{-crown-}$
18 $5)]^+$ based on DFT calculations. From the optimized solvation structures, the largest van der
19 Waals dimensions of these two solvated Li^+ ions can be estimated by fitting three-dimensional
20 ellipsoid surfaces that enclose all of the DFT-optimized coordinates for each of the solvents. We
21 obtain the largest dimension of 10.87 Å for $[\text{Li}(\text{TEGDME})]^+$ (ellipsoid axes: $a = 4.56$ Å, $b = 5.12$
22 Å, $c = 5.435$ Å) and 11.34 Å for $[\text{Li}(15\text{-crown-5})]^+$ (ellipsoid axes: $a = 3.51$ Å, $b = 5.24$ Å, $c =$
23 5.67 Å), respectively. Therefore, both solvated ions are smaller than the average van der Waals
24 diameter of EA-SWNTs (12.1 Å), but much larger than the average van der Waals diameter of
25 HiPco-SWNTs (6.6 Å).
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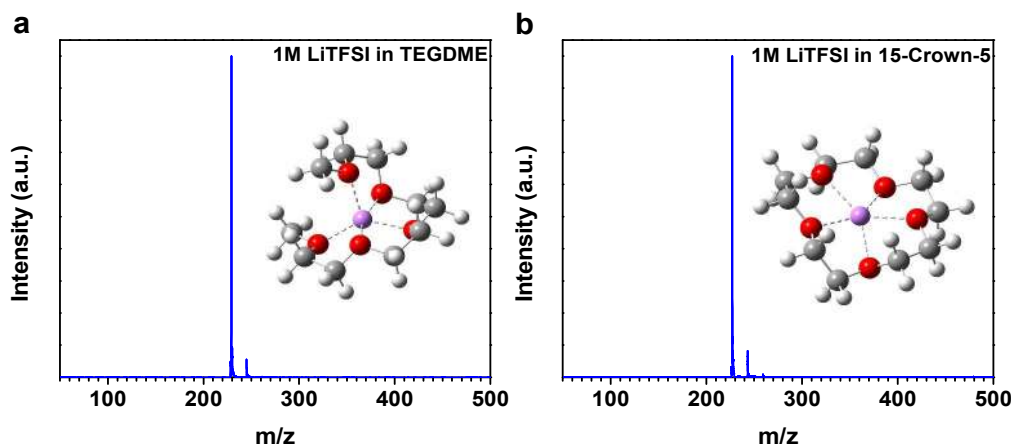


Figure 2. ESI-MS spectra of 1 M LiTFSI in (a) TEGDME and (b) 15-crown-5. The insets of each panel depict the DFT-optimized solvation structures.

The electrochemical properties of S@EA and S@HiPco with Li were characterized with CV and galvanostatic lithiation-delithiation in these two electrolytes. **Figures 3a** and **3b** show the CV (0.05 mV s^{-1}) and galvanostatic lithiation-delithiation (4 mA g^{-1}) curves, respectively, of S@EA in TEGDME and 15-crown-5 electrolytes vs. Li^+/Li . The CV scan in TEGDME electrolyte displays a series of cathodic peaks at 2.45 V, 2.13 V, and 1.97 V and two anodic peaks at 2.33 V and 2.5 V, which are consistent with its galvanostatic potential profile. The CV scan in 15-crown-5 displays more cathodic peaks at 2.65 V, 2.15 V, 1.8 V, 1.6 V, and 1.35 V, and correspondingly more anodic peaks at 1.9 V, 2.2 V, 2.4 V, and 2.65 V, which are also consistent with its galvanostatic potential profile. The CV and galvanostatic potential curves of S@EA in TEGDME electrolyte provide strong evidence that S@EA undergoes conventional solution-phase Li-S reactions involving Li polysulfides. The smaller size of solvated $[\text{Li}(\text{TEGDME})]^+$ ions compared to the EA-SWNTs diameter allows $[\text{Li}(\text{TEGDME})]^+$ ions to enter the EA-SWNTs with an excess of TEGDME molecules to react with the confined sulfur. In fact, the diameter of EA-SWNTs is large enough to accommodate both solvated $[\text{Li}(\text{TEGDME})]^+$ and $[\text{Li}(15\text{-crown-}$

5)]⁺ ions, enabling the conventional solution-phase Li-S electrochemical reaction in both electrolytes. The seemingly different electrochemical behaviors of Li-S@EA in 15-crown-5 may originate from the much higher viscosity of 15-crown-5 (21.7 cP at 25 °C)²⁴ than that of TEGDME (4.05 cP at 25 °C). The diffusion of Li polysulfides during the electrochemical process can be suppressed by the higher viscosity of 15-crown-5 and the restrictive 1-D SWNT confinement. The suppression of Li polysulfide dissolution improves the differentiation of the step-wise charge transfer processes in sulfur lithiation-delithiation, which typically could not be well distinguished in non-confined Li-S electrochemical reactions with CV or chronopotentiometry methods.

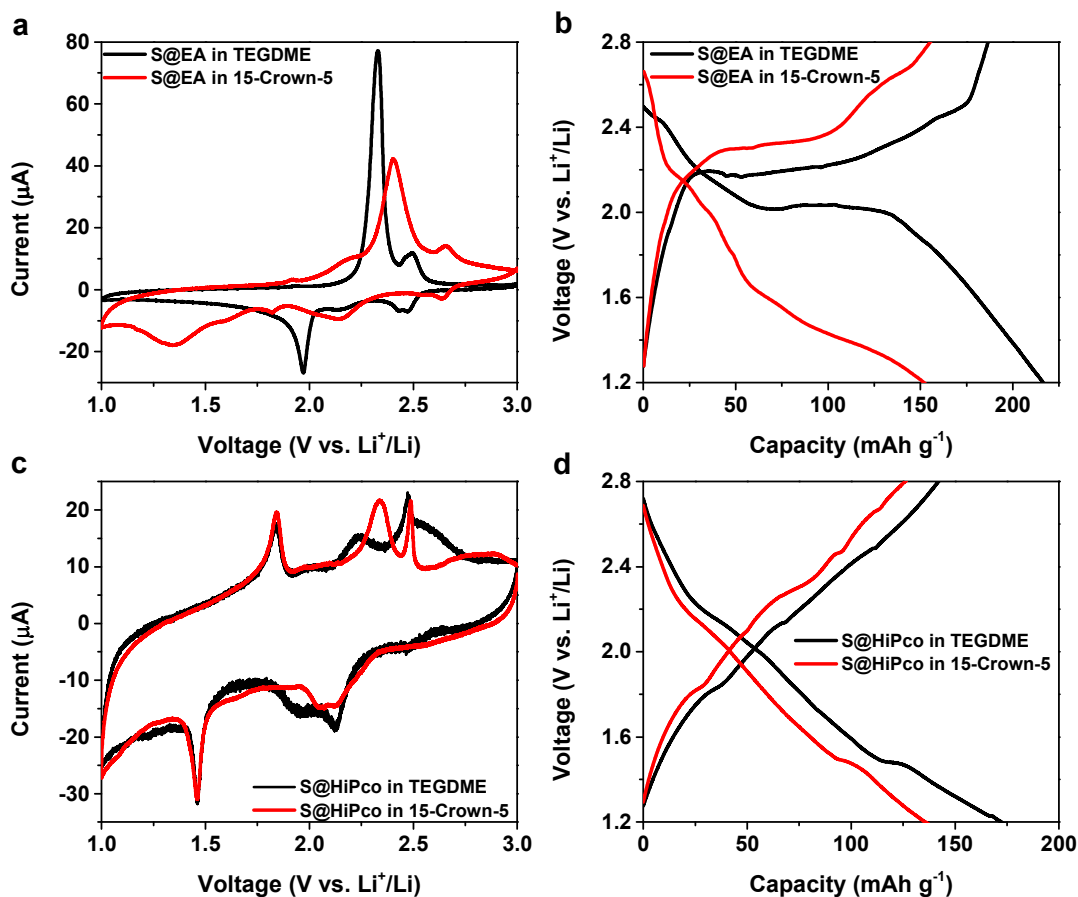


Figure 3. (a) CV and (b) galvanostatic lithiation-delithiation of S@EA in TEGDME and 15-crown-5; (c) CV and (d) galvanostatic lithiation-delithiation of S@HiPco in TEGDME and 15-

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3 crown-5. The scan rate of CV is 0.05 mV s^{-1} , and the current density of galvanostatic lithiation-
4 delithiation is 4 mA g^{-1} with respect to the total mass of S@SWNTs. The capacity is also based
5 on the mass of S@SWNTs.
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11 In sharp contrast, as shown in **Figures 3c** and **3d**, the electrochemical characteristics of
12 S@HiPco in TEGDME and 15-crown-5 electrolytes are not only fundamentally different from
13 those observed for S@EA, but also identical to each other. The CV scans of S@HiPco display
14 four cathodic peaks at 2.5 V (small in 15-crown-5), 2.12 V, 1.95 V, and 1.46 V, and three anodic
15 peaks at 1.85 V, 2.23 V (shifted to 2.33 V in 15-crown-5), and 2.48 V, which are consistent with
16 their galvanostatic potential profiles. The identical electrochemical behavior of S@HiPco in
17 TEGDME and 15-crown-5 electrolytes implies identical Li-S electrochemical mechanisms,
18 which cannot be explained by the conventional solution-phase Li-S electrochemical reaction. For
19 comparison, the CV scans of simple sulfur-HiPco-SWNT and sulfur-EA-SWNT mixtures in
20 TEGDME and 15-crown-5 electrolytes display conventional solution-phase Li-S electrochemical
21 behavior as shown in Figure S5 in Supporting Information. This new mechanism is very likely
22 due to the much smaller diameter of HiPco-SWNTs than that of EA-SWNTs. The inner van der
23 Waals diameter of HiPco-SWNTs is approximately 6.6 \AA , which can no longer accommodate
24 either of the solvated $[\text{Li}(\text{TEGDME})]^+$ and $[\text{Li}(15\text{-crown-5})]^+$ ions. It is worth noting that the
25 reaction between S@HiPco and Li is apparently different from the ones demonstrated in
26 microporous carbon¹⁻³ and with solid-state electrolytes,²⁵⁻²⁷ which are characterized with single
27 slope-like lithiation-delithiation curves and single pair redox peaks in CV. We hereby propose a
28 new mechanism: the solvated $[\text{Li}(\text{TEGDME})]^+$ and $[\text{Li}(15\text{-crown-5})]^+$ ions cannot enter the
29 interior of the HiPco-SWNTs; instead, the sulfur in S@HiPco is reduced through the SWNT wall
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via an out-of-plane π -electronic interaction, with Li^+ physically outside of SWNT but interacting with the π -orbitals of the sp^2 -carbon.

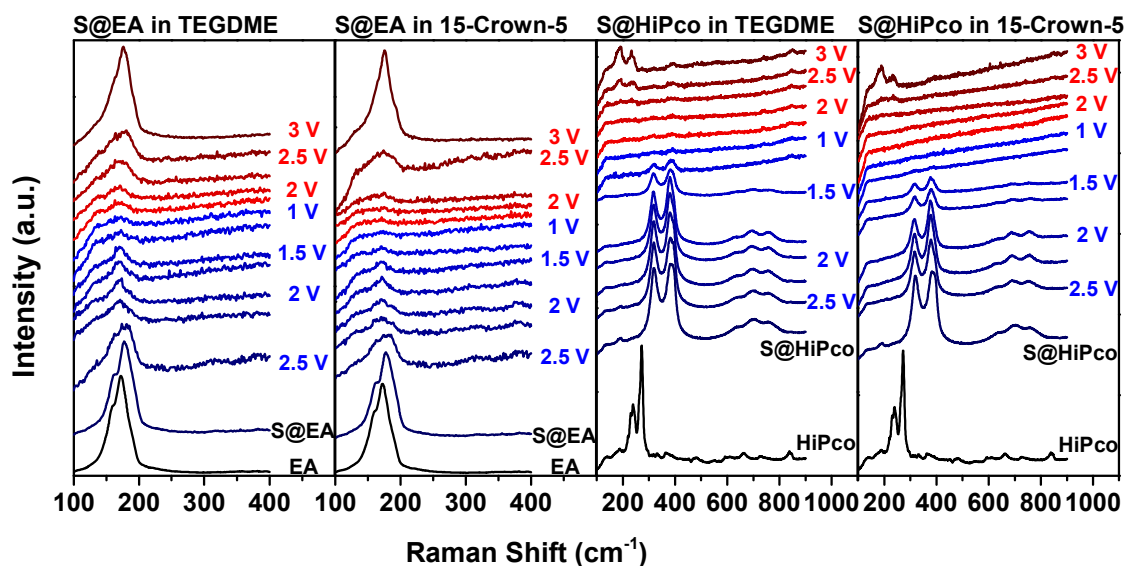


Figure 4. *Operando* Raman spectra showing the RBM region of S@EA and S@HiPco in both TEGDME and 15-crown-5 electrolytes during electrochemical lithiation-delithiation with a current density of 20 mA g^{-1} with respect to the total mass of S@SWNTs. Lithiation: 2.5 V to 1 V, delithiation: 1 V to 3 V vs. Li^+/Li .

The *operando* Raman spectroscopy also demonstrates the clear correlation between the Li-S electrochemical reactions and the diameters of the SWNTs. **Figure 4** displays the *operando* Raman spectra near the radial breathing mode (RBM) region of SWNTs obtained during the galvanostatic lithiation-delithiation of S@SWNTs in TEGDME and 15-crown-5 electrolytes, respectively. (The full *operando* Raman spectra are shown in Figure S6 in the Supporting Information). Due to the van der Waals interaction between the confined sulfur chains and the wall of the EA-SWNTs, the RBM Raman peak is slightly shifted from 172 cm^{-1} in EA-SWNTs to 178 cm^{-1} in S@EA-SWNTs, which is consistent with our previous finding.²² During lithiation,

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3 the RBM peak gradually redshifted back to 172 cm^{-1} with diminishing intensity. The shift of the
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5 peak indicates the weakening van der Waals interaction between the lithiated sulfur and the wall
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7 of the EA-SWNTs due to the cleavage of the long sulfur chains. The diminishment of the peak
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9 may indicate the formation of solid electrolyte interphase (SEI) or SEI-like species on the EA-
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11 SWNTs, which will be elaborated later in the analysis of the X-ray photoelectron spectroscopy
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13 (XPS) data. Another cause for the RBM peak diminishment in EA-SWNTs can be related to the
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15 Li to SWNT charge transfer (n-doping) resulting in bleaching of the optical interband transitions
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17 in the SWNTs and suppressing the resonance character of the Raman scattering. The reverse
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19 process can be observed in the spectra obtained during delithiation. After delithiation to 3 V, the
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21 RBM peak blue shifted to 175 cm^{-1} (lower than 178 cm^{-1} in the pristine S@EA), which indicates
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23 that sulfur was not fully converted back to the long chain structure in delithiation, resulting in a
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25 weaker interaction with the wall of the EA-SWNTs. Interestingly, the RBM peak also became
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27 more pronounced during delithiation, which may indicate the diminishing SEI-like species.
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34 The two right panels in Figures 4 depict the *operando* Raman spectra during the lithiation-
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36 delithiation of S@HiPco in TEGDME and 15-crown-5 electrolytes, respectively. The sulfur
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38 chains confined in HiPco-SWNTs have a stronger van der Waals interaction with the SWNT
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40 walls due to the narrower diameter resulting in the disappearance of the RBM peaks at 231 cm^{-1}
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42 and 272 cm^{-1} and an appearance of new Raman peaks at 315 cm^{-1} and 377 cm^{-1} originating from
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44 the molecular vibrations of encapsulated sulfur chains coupled with electronic excitations in
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46 SWNTs, as confirmed by the observed ^{32}S to ^{34}S isotopic shift.²² These new Raman peaks of
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48 S@HiPco gradually diminished during the lithiation but without a noticeable peak shift. The
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50 diminishment of these peaks may be due to the formation of SEI-like species in S@HiPco
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52 similar to that observed in S@EA and the suppression of the SWNT interband transitions due to
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Li to SWNT charge transfer.²² The absence of the peak shift may suggest that the reduction of confined sulfur (hypothetically *via* out-of-plane π -electronic interactions) does not alter the interaction with the wall. These new peaks completely disappear at the end of delithiation, while the Raman peaks in the RBM region at 188 cm^{-1} and 231 cm^{-1} are partially restored. Although the exact explanation of the Raman peak transformation in S@HiPco is unclear, the different *operando* Raman spectra can be unambiguously attributed to the narrower diameter of the HiPco-SWNTs than EA-SWNTs.

Table 1. The composition of the sulfur species in S@EA and S@HiPco calculated from XPS S 2p spectra at different lithiation-delithiation states in TEGDME and 15-crown-5 electrolytes, respectively.

| | | TEGDME | | | | | 15-Crown-5 | | | | |
|---|-------------------------|------------|-------|-------|--------------|-------|------------|-------|-------|--------------|-------|
| | | Lithiation | | | Delithiation | | Lithiation | | | Delithiation | |
| Potential (vs. Li^+/Li) | | 2.8 V | 2.0 V | 1.2 V | 2.3 V | 2.8 V | 2.8 V | 1.5 V | 1.2 V | 2.3 V | 2.8 V |
| S@EA | S % | 100 | 60.8 | 40.5 | 52.4 | 64.1 | 100 | 76.4 | 43.0 | 59.8 | 81.7 |
| | S²⁻ % | 0 | 39.2 | 59.5 | 47.6 | 35.9 | 0 | 23.6 | 57.0 | 40.2 | 18.3 |
| Potential (vs. Li^+/Li) | | 2.8 V | 1.5 V | 1.2 V | 2.3 V | 2.8 V | 2.8 V | 1.5 V | 1.2 V | 2.3 V | 2.8 V |
| S@HiPco | S % | 100 | 72.4 | 60.6 | 63.1 | 74.7 | 100 | 72.7 | 55.9 | 71.2 | 79.9 |
| | S²⁻ % | 0 | 27.6 | 39.4 | 36.9 | 25.3 | 0 | 27.3 | 44.1 | 28.8 | 20.1 |

The S@EA and S@HiPco at different states of lithiation-delithiation in TEGDME and 15-crown-5 electrolytes were further characterized with XPS. As shown in **Figure 5**, the S 2p spectra of pristine S@EA and S@HiPco both display S 2p_{3/2} and S 2p_{1/2} peaks of elemental sulfur at 164 eV and 165.2 eV. A small amount of the oxidized sulfur assigned to the peaks in the range of 166 eV to 171 eV in the pristine samples could be introduced during the sulfur infusion processes. The peaks of oxidized sulfur became more pronounced in the lithiated and delithiated samples due to the LiTFSI residue and possible [TFSI]⁻ anion decomposition.²⁸⁻³⁰ The

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3 XPS spectra indicate that all the lithiated and delithiated S@SWNTs contain two sulfur species:
4 elemental sulfur and lithium sulfide. These two species have different ratios at different
5 lithiation-delithiation states as listed in **Table 1**. It is worth noting that due to the spontaneous
6 disproportionation of Li polysulfides to elemental sulfur and Li₂S upon solvent removal,^{31,32} the
7 ratio of S/S²⁻ obtained from the *ex situ* XPS of S@EA only reflects the extent of lithiation-
8 delithiation, not necessarily the actual products in the electrochemical environment. On the
9 other hand, the sulfur and Li₂S species detected in S@HiPco are expectedly the actual products
10 based on the proposed reactions in S@HiPco *via* out-of-plane π -electronic interactions without
11 polysulfides.
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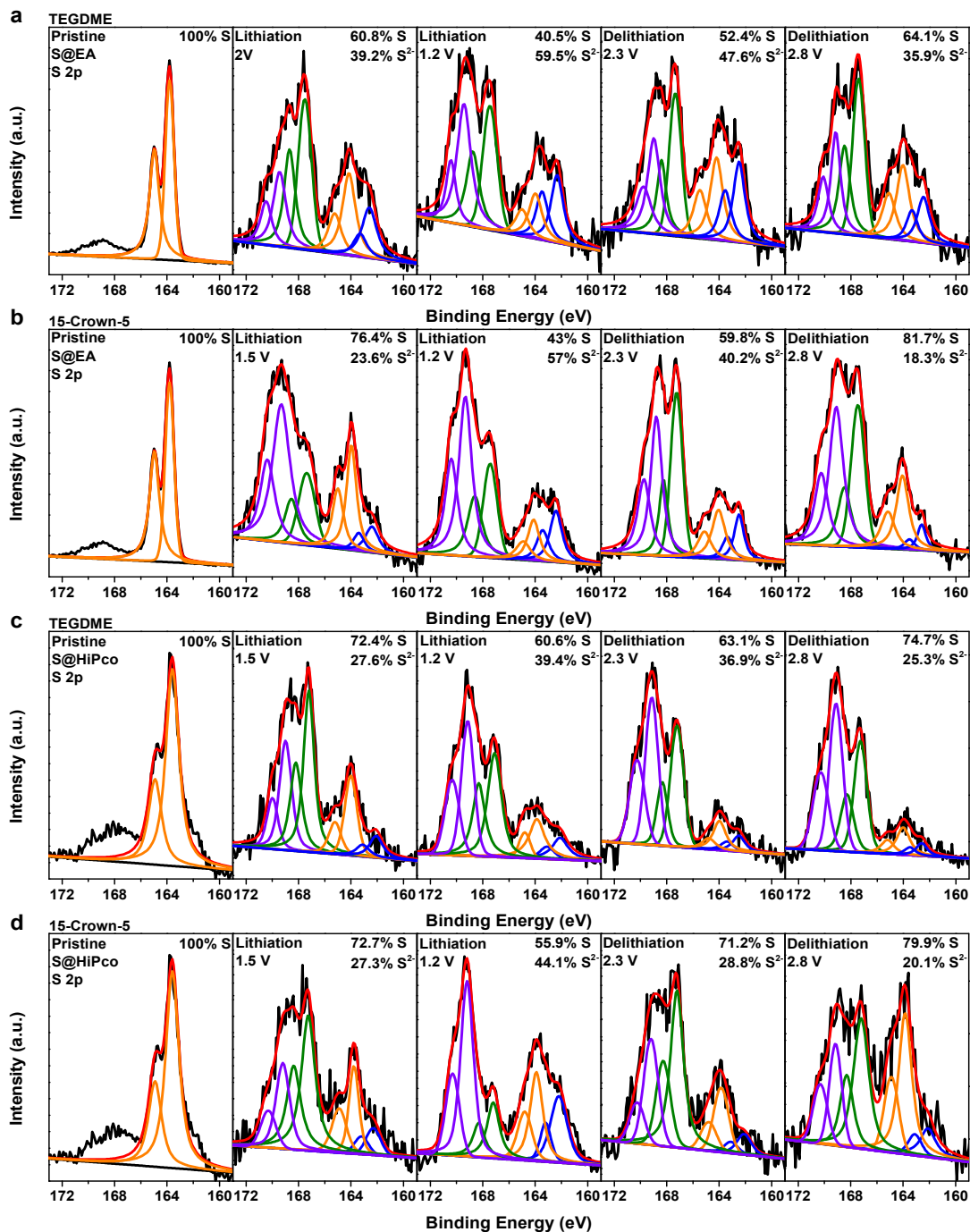


Figure 5. XPS S 2p spectra of (a, b) S@EA and (c, d) S@HiPco at different lithiation-delithiation states in TEGDME and 15-crown-5 electrolytes, respectively. The electrochemical lithiation-delithiation is performed with a current density of 20 mA g^{-1} with respect to the mass of S@EA and S@HiPco. Deconvolution color code: elemental sulfur peak: orange; oxidized sulfur species peaks: purple and green; Li_2S peak: blue.

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3 The most salient results from the S/S²⁻ ratio in the XPS is that the capacity of S@EA and
4 S@HiPco shown in **Figure 3** cannot be solely attributed to the lithiation-delithiation of sulfur.
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6 Based on the sulfur conversion in S@HiPco, the capacity contributed from sulfur lithiation is 82
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8 mAh g⁻¹ in TEGDME and 78 mAh g⁻¹ in 15-crown-5, suggesting that about 50% of the
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10 demonstrated capacity originates from a different mechanism (**Figure 3d**). The extra capacity in
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12 S@EA is also significant: lithiation of sulfur only contributes 45 mAh g⁻¹ to the total capacity of
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14 190 mAh g⁻¹ in TEGDME and 44 mAh g⁻¹ to the total capacity of 152 mAh g⁻¹ in 15-crown-5
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16 (**Figure 3b**). The extra capacity does not originate from the lithiation-delithiation of neat EA-
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18 SWNTs and HiPco-SWNTs, which displays negligible capacity (Figure S7 in the Supporting
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20 Information). The *ex situ* XPS C 1s spectra of the lithiated and delithiated S@EA and S@HiPco
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22 sheds some light on the origin of the extra capacity: As shown in **Figures 6a** and **6b**, the spectra
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24 of the pristine S@EA and S@HiPco both indicate the existence of a C-C bond at 284.5 eV (blue
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26 curve), a C-O bond at 285.5 eV (green curve), and an isolated carbonyl C=O bond at 287 eV
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28 (purple curve). The latter two may arise from the impurity of the pristine SWNTs or impurities
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30 introduced during the sulfur encapsulation. During lithiation, both C-O and C=O peaks become
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32 much more pronounced by using the C-C peak at 284.5 eV as a reference. In addition, a strong
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34 peak representing carboxylic acid ester group (O=C-O) appears at 289.5 eV (orange) in
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36 lithiation. This observation indicates the formation of possible species including C-O-Li and
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38 O=C-O-Li due to the TEGDME and 15-crown-5 decomposition *via* electrochemical reduction in
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40 the present of Li⁺ ions.^{33,34} These observations are consistent with the indication from the
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42 *operando* Raman results displayed in **Figure 6c**. Both S@EA and S@HiPco in either electrolyte
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44 clearly demonstrate decreasing the G-band peak (1580 cm⁻¹) and increasing the D-band peak
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46 (1350 cm⁻¹) during lithiation and the reverse trend during delithiation. Such reactions apparently
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3 do not occur under the same condition with pure EA-SWNTs and HiPco-SWNTs. Therefore,
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5 S@EA and S@HiPco nanostructures may possess catalytic activity to facilitate the formation of
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7 these species. After delithiation, the intensity of the peaks at 289.5 eV (O=C-O-Li), 287 eV
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9 (C=O), and 285.5 (C-O-Li) all significantly decrease in comparison to the C-C peak at 284.5 eV,
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11 which suggests the decomposition of the SEI-like layer under an electrochemical oxidation
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13 environment. The reversibility of these SEI-like species was still observed after 10 cycles in the
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15 XPS C 1s spectra (Figure S8 in Supporting Information).
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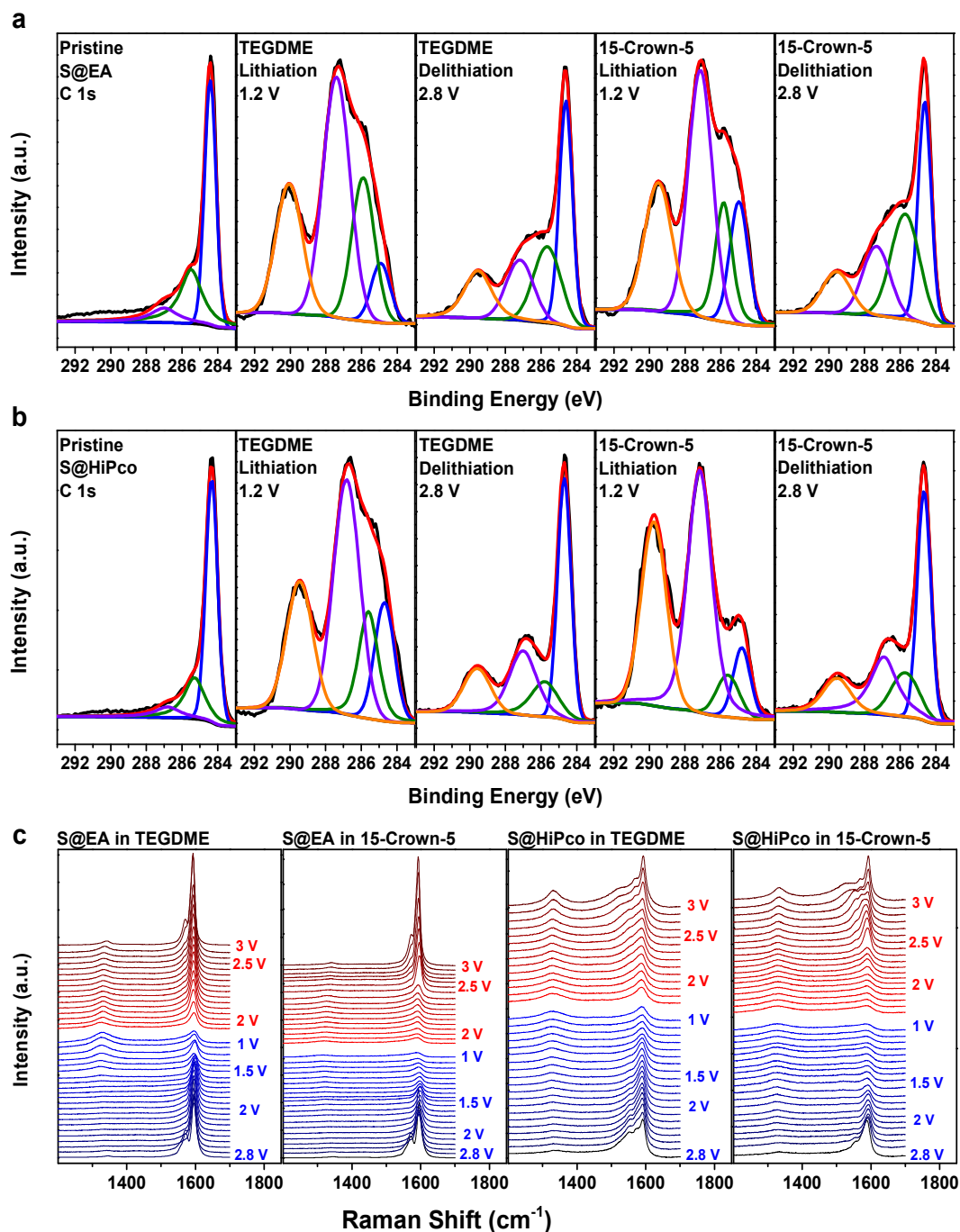
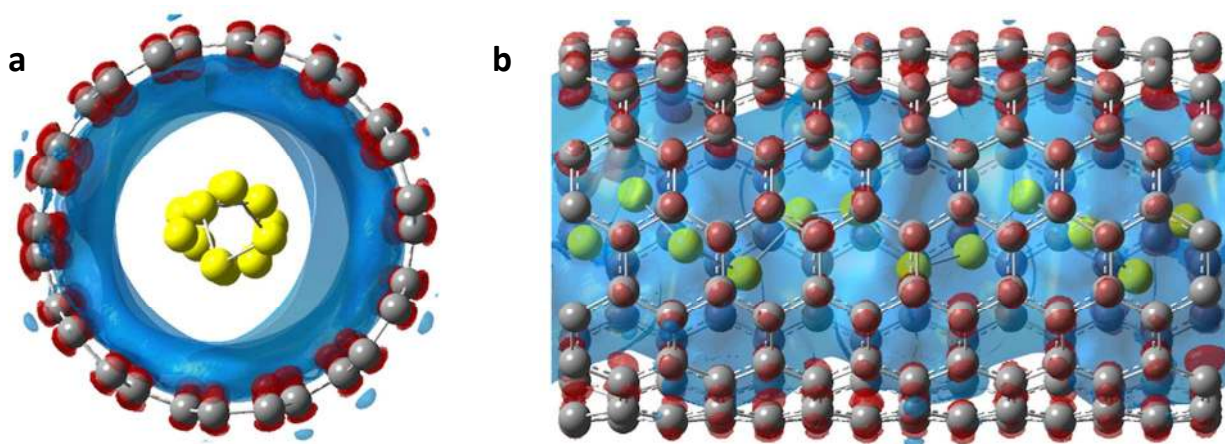


Figure 6. XPS C 1s spectra of (a) pristine S@EA, lithiated and delithiated S@EA in TEGDME and 15-crown-5 electrolytes and (b) pristine S@HiPco, lithiated and delithiated S@HiPco in TEGDME and 15-crown-5 electrolytes; (c) *operando* Raman spectra in the D-band and G-band region of S@EA and S@HiPco during lithiation-delithiation (lithiation: 2.8 V to 1 V, delithiation: 1 V to 3 V). XPS deconvolution color code: C-C peak: blue; C-O peak: green; C=O peak: purple; O=C-O peak: orange.

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3 The reversible formation and decomposition of the SEI-like layer, facilitated by the hypothesized
4 catalytic activity of S@EA and S@HiPco, clearly contribute to the extra capacity during
5 lithiation-delithiation. Indeed, our large-scale DFT calculations on these nanostructures
6 corroborate the proposed catalytic activity by showing that a significant dynamic electron
7 transfer occurs from the encapsulated sulfur to the surrounding SWNT/electrolyte. **Figure 7**
8 depicts the electron density difference ($\Delta\rho = \rho_{\text{S@SWNT}} - \rho_{\text{SWNT}}$)³⁵ for a (7,7) S@SWNT
9 computed with dispersion-corrected DFT.³⁶ As depicted below, $\Delta\rho$ gives a dynamic visualization
10 of electronic rearrangement when sulfur is encapsulated within the SWNT: red regions denote an
11 accumulation of electron density (primarily around the SWNT) and blue regions represent a
12 depletion of density (from the sulfur). The amount of charge transfer is quite sizeable with 0.37
13 e^- being transferred from the sulfur to the SWNT within the unit cell depicted in **Figure 7**. Most
14 notably, our DFT calculations show similar trends with other SWNT chiralities (such as the
15 (10,0) semiconducting SWNT) as well as S@SWNT geometries in the presence of a surrounding
16 electrolyte (Figure S9 in the Supporting Information).
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52 **Figure 7.** Electron density difference maps ($\Delta\rho = \rho_{\text{S@SWNT}} - \rho_{\text{SWNT}}$) for a (7,7) S@SWNT
53 viewed along the (a) axis and (b) side length as computed with dispersion-corrected DFT. Red
54 regions denote an accumulation of electron density (compared to the bare SWNT), and blue
55 regions represent a depletion of electron density.
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Conclusions

In summary, we have investigated the chemical properties of sulfur confined in EA-SWNTs and HiPco-SWNTs, and we demonstrate an unusual electrochemical reactivity of sulfur upon encapsulation in narrow-diameter (sub-nano) SWNTs with lithium. Our findings are corroborated and supported with various spectroscopic analyses including *operando* Raman, X-ray photoelectron spectroscopy, and first-principles calculations from density functional theory. Collectively, these results show that electrochemical properties can be dramatically modulated by varying the diameter of the SWNTs and the dimension of the solvated Li^+ ions. Specifically, the relatively large diameter of EA-SWNTs accommodates solvated Li^+ ions so that solution-phase Li-S reactions can occur within the interior of EA-SWNTs. In contrast, the narrower diameter of HiPco-SWNTs prevents solvated Li^+ ions from entering the interior. As a result, the Li-S reaction in HiPco-SWNTs is markedly different and proposed to occur *via* a through-wall π -electronic interaction. Our combined spectroscopic and DFT analyses also suggest a formation-decomposition mechanism of SEI-like species facilitated by the catalytic activity of the S@SWNTs, which is induced by the sulfur-SWNT interactions in this nano-chemical environment. This finding provides an exciting opportunity that can be further leveraged to probe fundamental chemical reaction mechanisms of S@SWNTs as energy storage or electrocatalytic materials.

Methods/Experimental

Preparation of S@SWNTs: SWNTs (EA-SWNTs obtained from Carbon Solutions, Inc. and HiPco-SWNTs purchased from NanoIntegris) and sulfur (99.99%, Sigma-Aldrich) were sealed

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3 in a vacuum hourglass-shaped quartz tube as shown in **Figure S10** in the Supporting
4 Information. SWNTs were loaded in the top compartment, and sulfur was loaded in the bottom
5 one. The sealed tube was placed vertically in a muffle furnace for heat treatment at 600 °C for 48
6 hours. Under the experimental conditions, the sulfur in the sealed tube reached vapor-liquid
7 phase equilibrium. Therefore, the SWNTs were exposed to saturated sulfur vapor without contact
8 with liquid sulfur. After the heat treatment, the obtained materials were further heated at 350 °C
9 in flowing argon for 10 hours to completely remove the sulfur deposited on the exterior of
10 SWNTs.
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21 **Microscopic Characterization:** The samples were dispersed in DMF by ultrasonication with a 5
22 s pulse on and a 10 s pulse off at room temperature for 2 h, and then dropped onto TEM grids.
23 HRTEM imaging was performed on an aberration-corrected and monochromated G2 cubed Titan
24 60-300 electron microscope under 60 kV. Scanning transmission electron microscopy (STEM)
25 was performed with an aberration-corrected Nion UltraSTEM 100 at Oak Ridge National
26 Laboratory, which is equipped with a second generation 5th order probe aberration corrector, a
27 cold field emission electron gun, and a Gatan Enfina Energy Loss Spectrometer. Imaging was
28 performed at 60 keV, below the knock-on threshold for carbon atoms, to minimize damage on
29 SWNTs using a semi-convergence angle of 30 mrad and an inner semi-angle of 54 mrad for the
30 annular dark field detector. EEL spectroscopy and spectrum imaging was performed
31 simultaneously with imaging and with a dispersion of 0.1eV/channel.
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47 **Electrochemical Characterization:** The electrodes were composed of 90 wt. % of S@SWNTs
48 (or pure SWNTs) and 10 wt. % of polyvinylpyrrolidone (Sigma-Aldrich) binder. The areal
49 loading of S@SWNTs or pure SWNTs is approximately 2 mg cm⁻². Aluminum foil (99.45%,
50 Alfa Aesar) was used as the current collector. Two-electrode coin cells with lithium foil (Alfa
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3 Aesar) as the counter electrode were assembled in an argon-filled glovebox for the
4 electrochemical analysis. Electrolytes consisting of 1 M LiTFSI (Sigma-Aldrich) in TEGDME
5 (Sigma-Aldrich) and 15-crown-5 (Sigma-Aldrich) were used with a porous membrane separator
6 (Celgard 2500). The cells were charged and discharged with different cycling currents between 1
7 and 3 V (vs. Li^+/Li) using an Arbin battery test station. CV scans were performed on a Gamry
8 Interface 1000 analyzer.
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12 **Operando Raman Spectroscopy:** 2 mg S@SWNTs were dispersed in 100 mL of
13 dimethylformamide by sonication for 5 h. The dispersion was centrifuged at 8000 rpm (11,000 g)
14 for 15 min. The obtained supernatant was then filtered through a porous membrane (Celgard
15 2500), which was also used as the separator in the cells for the *operando* Raman study. The
16 S@SWNTs film coated membrane (**Figure S11** in the Supporting Information) was used as the
17 positive electrode in the modified cell for *Operando* Raman measurement. A coin cell case with
18 a Kapton window on the positive side was purchased from MTI Corporation. The Kapton film
19 was cut off, and a thin transparent glass slide was attached on the cell case using a Frame-Seal
20 tape (Bio-rad). The cells were assembled in an argon-filled glovebox with the S@SWNTs film
21 facing the glass window (**Figure S12** in the Supporting Information). The cells were mounted
22 onto a Raman microscope (Nicolet Almega XR with 532 nm wavelength laser source) with the
23 window facing the laser source. The cells were lithiated and delithiated at a current density of 20
24 mA g^{-1} with a Gamry Reference 3000 analyzer, while the Raman spectra was collected every 10
25 minutes.
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30 **X-ray Photoelectron Spectroscopy:** The cells were discharged or charged to a certain potential
31 and disassembled in an argon-filled glovebox. The S@SWNTs electrodes were washed with
32 dimethoxyethane for 3 times to remove the electrolyte residual and dried at room temperature in
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3 the glovebox for 48 hours. The chemical state of sulfur and carbon in the S@SWNTs was
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5 characterized with XPS (AXIS Supra) at the Irvine Materials Research Institute at University of
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7 California - Irvine. An inert gas-filled glove box is attached to the Supra's UHV preparation
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9 chamber so the samples were not exposed to the ambient environment.
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12 **DFT Computational Methods:** Geometry optimizations of a (7,7) SWCNT filled with sulfur
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14 were carried out with the VASP code using a plane-wave basis and periodic boundary conditions,
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16 where the projector augmented wave (PAW) method was used to numerically represent the
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18 electron wave functions. We used the nonlocal optB86b-vdW exchange-correlation functional
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20 which explicitly calculates van der Waals effects (via nonlocal double real-space integrals of the
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22 electron density) to account for the dispersion interactions between the SWNT and the sulfur
23
24 chain. A 4x1x1 mesh of k points was implemented for the Brillouin zone integration, and a 402
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26 eV energy cutoff was used for the electronic wavefunctions. A vacuum region of ~ 30 Å was
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28 used in the y and z -direction, and periodic boundary conditions were applied in all three
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30 dimensions.
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39 ASSOCIATED CONTENT

41 **Supporting Information.**

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45 The Supporting Information is available free of charge on the ACS Publications website at DOI:

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51 Experimental details, sulfur content analysis *via* colorimetric titration, EDX and EELS of S@EA
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53 and S@HiPco SWNTs, additional HRTEM images of S@HiPco SWNTs, DFT optimizations
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55 and geometric analyses of S@SWNTs, CV of simple mixture of sulfur with EA-SWNTs and
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3 HiPco-SWNTs in TEGDME and 15-crown-5 electrolytes, full *operando* Raman spectra,
4 galvanostatic lithiation-delithiation of pure EA-SWNTs and HiPco-SWNTs, XPS C 1s spectra
5 after 10 lithiation-delithiation cycles, DFT S@SWNT geometries in the presence of a
6 surrounding electrolyte, digital images of the vacuum vessel for sulfur infusion, S@SWNT
7 electrode, and modified cell for *operando* Raman experiments.
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8 9 DEDICATION

10 Dedicated to our dear colleague and friend Prof. Robert C. Haddon.
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13 14 REFERENCES

15
16
17 (1) Fu, C. Y.; Wong, B. M.; Bozhilov, K. N.; Guo, J. C. Solid State Lithiation-delithiation of
18
19 Sulphur in Sub-nano Confinement: A New Concept for Designing Lithium-Sulphur Batteries.
20
21 *Chem. Sci.* **2016**, 7, 1224–1232.
22
23

24
25 (2) Wang, D.-W.; Zhou, G. M.; Li, F.; Wu, K.-H.; Lu, G. M.; Cheng, H.-M.; Gentle, I. A
26
27 Microporous-Mesoporous Carbon with Graphitic Structure for a High-Rate Stable Sulfur
28
29 Cathode in Carbonate Solvent-Based Li-S Batteries. *Phys. Chem. Chem. Phys.* **2012**, 14, 8703–
30
31 8710.
32
33

34
35 (3) Li, Z.; Yuan, L.; Yi, Z.; Sun, Y.; Liu, Y.; Jiang, Y.; Shen, Y.; Xin, Y.; Zhang, Z.; Huang, Y.
36
37 Insight into the Electrode Mechanism in Lithium-Sulfur Batteries with Ordered Microporous
38
39 Carbon Confined Sulfur as the Cathode. *Adv. Energy Mater.* **2014**, 4, 1301473.
40
41

42
43 (4) Xin, S.; Gu, L.; Zhao, N.-H.; Yin, Y.-X.; Zhou, L.-J.; Guo, Y.-G.; Wan, L.-J. Smaller Sulfur
44
45 Molecules Promise Better Lithium-Sulfur Batteries. *J. Am. Chem. Soc.* **2012**, 134, 18510–18513.
46
47

48
49 (5) Zhang, S. S. Sulfurized Carbon: A Class of Cathode Materials for High Performance
50
51 Lithium/Sulfur Batteries. *Front. Energy Res.* **2013**, 1, 1–9.
52
53

1
2
3 (6) Markevich, E.; Salitra, G.; Rosenman, A.; Talyosef, Y.; Chesneau, F.; Aurbach, D. The
4 Effect of A Solid Electrolyte Interphase on the Mechanism of Operation of Lithium-Sulfur
5 Batteries. *J. Mater. Chem. A* **2015**, *3*, 19873–19883.
6
7

8
9
10
11 (7) Markevich, E.; Salitra, G.; Talyosef, Y.; Chesneau, F.; Aurbach, D. Review—On the
12 Mechanism of Quasi-Solid-State Lithiation of Sulfur Encapsulated in Microporous Carbons: Is
13 the Existence of Small Sulfur Molecules Necessary? *J. Electrochem. Soc.* **2017**, *164*, A6244-
14 A6253.
15
16
17
18

19
20
21 (8) Smith, B. W.; Monthieux, M.; Luzzi, D. E. Encapsulated C60 in Carbon Nanotubes. *Nature*
22 **1998**, *396*, 323-324.
23
24
25

26
27 (9) Kataura, H.; Maniwa, Y.; Kodama, T.; Kikuchi, K.; Hirahara, K.; Suenaga, K.; Lijima, S.;
28 Suzuki, S.; Achiba, Y.; Krätschmer, W. High-Yield Fullerene Encapsulation in Single-Wall
29 Carbon Nanotubes. *Synthetic Metals* **2001**, *121*, 1195-1196.
30
31
32
33

34 (10) Monthieux, M. Filling Single-Wall Carbon Nanotubes. *Carbon* **2002**, *40*, 1809-1823.
35
36
37

38 (11) Khlobystov, A. N.; Britz, D. A.; Briggs, G. A. D. Molecules in Carbon Nanotubes. *Acc.*
39 *Chem. Res.* **2005**, *38*, 901-909.
40
41
42

43 (12) Medeiros, P. V. C.; Marks, S.; Wynn, J. M.; Vasylenko, A.; Ramasse, Q. M.; Quigley, D.;
44 Sloan, J.; Morris A. J. Single-Atom Scale Structural Selectivity in Te Nanowires Encapsulated
45 Inside Ultranarrow, Single-Walled Carbon Nanotubes. *ACS Nano* **2017**, *11*, 6178–6185.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 (13) Hart, M.; White, E. R.; Chen, J.; McGilvery, C. M.; Pickard, C. J.; Michaelides, A.; Sella,
4 A.; Shaffer, M. S. P.; Salzmann, C. G. Encapsulation and Polymerization of White Phosphorus
5 Inside Single-Wall Carbon Nanotubes. *Angew. Chem.* **2017**, *56*, 8144–8148.
6
7

8
9
10 (14) Komsa, H.-P.; Senga, R.; Suenaga, K.; Krasheninnikov A. V. Structural Distortions and
11 Charge Density Waves in Iodine Chains Encapsulated inside Carbon Nanotubes. *Nano Lett.*
12 **2017**, *17*, 3694–3700.
13
14
15

16
17 (15) Botos, A.; Biskupek, J.; Chamberlain, T. W.; Rance, G. A.; Stoppiello, C. T.; Sloan, J.; Liu,
18 Z.; Suenaga, K.; Kaiser, U.; Khlobystov, A. N. Carbon Nanotubes as Electrically Active
19 Nanoreactors for Multi-Step Inorganic Synthesis: Sequential Transformations of Molecules to
20 Nanoclusters and Nanoclusters to Nanoribbons. *J. Am. Chem. Soc.* **2016**, *138*, 8175–8183.
21
22
23
24
25

26 (16) Eliseev, A. A.; Chernysheva, M. V.; Verbitskii, N. I.; Kiseleva, E. A.; Lukashin, A. V.;
27 Tretyakov, Y. D.; Kiselev, N. A.; Zhigalina, O. M.; Zakalyukin, R. M.; Vasiliev, A. L.;
28 Krestinin, A. V.; Hutchison, J. L.; Freitag, B. Chemical Reactions within Single-Walled Carbon
29 Nanotube Channels. *Chem. Mater.* **2009**, *21*, 5001–5003.
30
31
32
33
34
35
36

37 (17) Takenobu, T.; Takano, T.; Shiraishi, M.; Murakami, H.; Ata, M.; Kataura, H.; Achiba, Y.;
38 Iwasa, Y. Stable and Controlled Amphoteric Doping by Encapsulation of Organic Molecules
39 inside Carbon Nanotubes. *Nat. Mater.* **2003**, *2*, 683-688.
40
41
42
43
44
45
46

47 (18) Castillejos, E.; Debouttière, P. J.; Roiban, L.; Solhy, A.; Martinez, V.; Kihn, Y.; Ersen, O.;
48 Philippot, K.; Chaudret, B.; Serp, P. An Efficient Strategy to Drive Nanoparticles into Carbon
49 Nanotubes and the Remarkable Effect of Confinement on Their Catalytic Performance. *Angew.*
50 *Chem.* **2009**, *121*, 2567-2571.
51
52
53
54
55
56
57
58
59
60

1
2
3 (19) Pan, X.; Bao, X. The Effects of Confinement inside Carbon Nanotube on Catalysis. *Acc.*
4
5 *Chem. Res.* **2011**, 44, 553-650.
6

7
8 (20) Fujimori, T.; Morelos-Gómez, A.; Zhu, Z.; Muramatsu, H.; Futamura, R.; Urita, K.;
9
10 Terrones, M.; Hayashi, T.; Endo, M.; Hong, S. Y.; Choi, Y. C.; Tomanek, D.; Kaneko, K.
11
12 Conducting Linear Chains of Sulphur Inside Carbon Nanotubes. *Nat. Commun.* **2013**, 4, 3162.
13
14

15
16 (21) Yang C.-P., Yin Y.-X., Guo Y.-G., and Wan L.-J. Electrochemical (De)Lithiation of 1D
17
18 Sulfur Chains in Li-S Batteries: A Model System Study. *J. Am. Chem. Soc.* **2015**, 137, 2215–
19
20 2218.
21
22

23
24 (22) Li, G.; Fu, C.; Oviedo, M. B.; Chen, M.; Tian, X.; Bekyarova, E.; Itkis, M. E.; Wong, B.
25
26 M.; Guo, J.; Haddon, R. C. Giant Raman Response to the Encapsulation of Sulfur in Narrow
27
28 Diameter Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2016**, 138, 40–43.
29
30

31
32 (23) Chemistry of the Elements (2nd Edition) N. N. Greenwood A. Earnshaw, Butterworth-
33
34 Heinemann. ISBN: 9780750633659
35
36

37
38 (24) Weast, R. C.; Astle, M. J. CRC Handbook of Chemistry and Physics, 62nd ed.; CRC Press:
39
40 Boca Raton, FL, 1981.
41
42

43
44 (25) Lin, Z.; Liu, Z.; Dudney, N. J.; Liang, C. Lithium Superionic Sulfide Cathode for All-Solid
45
46 Lithium-Sulfur Batteries. *ACS Nano* **2013**, 7, 2829–2833.
47
48

49
50 (26) Lin, Z.; Liu, Z.; Fu, W.; Dudney, N. J.; Liang, C. Lithium Polysulfidophosphates: A Family
51
52 of Lithium-Conducting Sulfur-Rich Compounds for Lithium-Sulfur Batteries. *Angew. Chem.,*
53
54 *Int. Ed.* **2013**, 52, 7460–7463.
55
56

- 1
2
3 (27) Han, F.; Yue, J.; Fan, X.; Gao, T.; Luo, C.; Ma, Z.; Suo, L.; Wang, C. High-Performance
4 All-Solid-State Lithium-Sulfur Battery Enabled by a Mixed-Conductive Li_2S Nanocomposite.
5
6 *Nano Lett.* **2016**, 16, 4521–4527.
7
8
9
10
11 (28) Fu, Y.; Zu, C.; Manthiram, A. *In Situ*-formed Li_2S in Lithiated Graphite Electrodes for
12 Lithium–Sulfur Batteries. *J. Am. Chem. Soc.* **2013**, 135, 18044–18047.
13
14
15
16 (29) Su, Y.-S.; Fu, Y.; Cochell, T.; Manthiram, A. A Strategic Approach to Recharging Lithium-
17 Sulphur Batteries for Long Cycle Life. *Nat. Commun.* **2013**, 4, 2985–2992.
18
19
20
21
22 (30) Tao, X.; Wang, J.; Ying, Z.; Cai, Q.; Zheng, G.; Gan, Y.; Huang, H.; Xia, Y.; Liang, C.;
23 Zhang, W.; Cui, Y. Strong Sulfur Binding with Conducting Magnéli-Phase $\text{Ti}_n\text{O}_{2n-1}$
24 Nanomaterials for Improving Lithium–Sulfur Batteries. *Nano Lett.* **2014**, 14, 5288–5294.
25
26
27
28
29
30 (31) Sharma, R. A. Equilibrium Phases in the Lithium-Sulfur System. *J. Electrochem. Soc.* **1972**,
31 119, 1439-1443.
32
33
34
35 (32) Cunningham P. T.; Johnson S. A.; Cairns, E. J. Phase Equilibria in Lithium–Chalcogen
36 Systems II. Lithium-Sulfur. *J. Electrochem. Soc.* **1972**, 119, 1448-1450.
37
38
39
40
41 (33) Islam, M. M.; Bryantsev, V. S.; Duin A. C. T. ReaxFF Reactive Force Field Simulations on
42 the Influence of Teflon on Electrolyte Decomposition during Li/SWCNT Anode Discharge in
43 Lithium-Sulfur Batteries. *J. Electrochem. Soc.* **2014**, 161, E3009-E3014.
44
45
46
47
48
49 (34) Assary, R. S.; Curtiss, L. A.; Moore, J. S. Toward a Molecular Understanding of Energetics
50 in Li–S Batteries Using Nonaqueous Electrolytes: A High-Level Quantum Chemical Study. *J.*
51 *Phys. Chem. C* **2014**, 118, 11545–11558.
52
53
54
55
56
57
58
59
60

1
2
3 (35) Wong, B. M.; Hsieh, T. H. Optoelectronic and Excitonic Properties of Oligoacenes:
4 Substantial Improvements from Range-Separated Time-Dependent Density Functional Theory. *J.*
5
6
7
8 *Chem. Theory Comput.* **2010**, 6, 3704–3712.

9
10
11 (36) Joo, Y.; Kim, M.; Huang, P.; Kanimozhi, C.; Wong, B. M.; Roy, S. S.; Arnold, M. S.;
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
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41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Gopalan, P. Effect of Dipolar Molecule Structure on the Mechanism of Graphene-Enhanced
Raman Scattering. *J. Phys. Chem. C* **2016**, 120, 13815–13824.

