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# Surface Chemistry in Cobalt Phosphide-Stabilized Lithium-**Sulfur Batteries**

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**ABSTRACT:** Chemistry at the cathode/electrolyte interface plays an important role for lithium-sulfur batteries in which stable cycling of the sulfur cathode requires confinement of the lithium polysulfide intermediates and their fast electrochemical conversion on the electrode surface. While many materials have been found to be effective for confining polysulfides, the underlying chemical interactions remain poorly understood. We report a new and general lithium polysulfide-binding mechanism enabled by surface oxidation layers of transition metal phosphide and chalcogenide materials. We for the first time find that CoP nanoparticles strongly adsorb polysulfides because their natural oxidation (forming Co-O-P-like species) activates the surface Co sites for binding polysulfides via strong Co-S bonding. With a surface oxidation layer capable of confining polysulfides and an inner core suitable for conducting electrons, the CoP nanoparticles are thus a desirable candidate for stabilizing and improving the performance of sulfur cathodes in lithium-sulfur batteries. We demonstrate that sulfur electrodes that hold a high mass loading of 7 mg cm<sup>-2</sup> and a high areal capacity of 5.6 mAh cm<sup>-2</sup> can be stably cycled for 200 cycles. We further reveal that this new surface oxidation-induced polysulfide-binding scheme applies to a series of transition metal phosphide and chalcogenide materials and can explain their stabilizing effects for lithium-sulfur batteries.

#### INTRODUCTION

The growing demand on energy storage technology for large scale applications such as electrical vehicles and smart grids drives the exploration of next-generation batteries to replace the current lithium ion batteries (LIBs).<sup>1-2</sup> As a promising candidate, lithium-sulfur batteries (LSBs) carry an attractive specific energy of 2600 Wh kg<sup>-1</sup>, 5 times higher than that of the state-of-the-art LIBs.<sup>3-5</sup> However, the present LSBs are still subject to pronounced capacity fading over long-term cycling. One of the major causes to the short cycle life problem is the dissolution and diffusion of the lithium polysulfide (LPS) intermediates, which can result in active material loss and structural changes on the sulfur cathode as well as degradation of the lithium anode.<sup>6-12</sup>

Using polarized material surfaces to confine LPS via chemical interactions has emerged as one of the most effective ways of improving the cycling stability of sulfur cathodes.<sup>13-22</sup> For example, utilizing NiFe<sub>2</sub>O<sub>4</sub> nanosheets as a LPS confining agent, we achieved a stable cycling performance for over 500 charging-discharging cycles with a capacity decay rate as low as ~0.009% per cycle.<sup>23</sup> It has been identified that 3d transition metal oxides interact with LPS via dominant oxygenlithium binding and minor metal-sulfur binding.<sup>24</sup> Recently, we have reported that transition metal phosphides, with their strong affinity for adsorbing LPS and good electronic conductivity for promoting electrochemical redox conversion of LPS, are even better at stabilizing sulfur cathodes.<sup>25</sup> Despite the superior performance, it remains poorly understood how metal phosphides chemically interact with LPS at the solid/liquid interface, which is preventing molecular-level understanding ACS Paragon Plus Environment

of the LSB surface chemistry and rational design of highperformance cathode materials for better LSBs.

Here we report a new surface chemistry phenomenon for LSB cathodes containing CoP nanoparticles and demonstrate the utilization of the distinct phenomenon to improve battery cycle life. We have discovered that the strong binding of CoP nanoparticles to LPS originates from the oxidation layer generated on the nanoparticle surface under ambient conditions. Surface oxidation creates Co-O-P species and thus activates the Co sites for chemically binding the negatively charged S sites of LPS. In contrast, nearly-pristine CoP nanoparticles with a reduced surface hardly bind or adsorb any LPS. Existence of the surface oxidation layer unlocks the potential of CoP nanoparticles for adsorbing and electrochemically converting LPS. High-capacity and stable-cycling sulfur cathodes are thus achieved. Our sulfur electrode incorporating CoP nanoparticles delivers a high and stable areal capacity of ~5.6 mAh cm<sup>-2</sup> for 200 cycles. We further recognize that this surface oxidation-induced LPS binding phenomenon exists for a number of transition metal phosphides and chalcogenides such as MoP, Ni<sub>2</sub>P, FeP, CoS and CoSe<sub>2</sub>. Our results highlight the importance of understanding the surface chemistry at the cathode/electrolyte interface in LSBs.

#### **RESULTS AND DISCUSSION**

CoP nanoparticles were grown on mildly-oxidized multiwall carbon nanotubes  $(CNTs)^{26-27}$  with a sequential synthesis method in which Co<sub>3</sub>O<sub>4</sub> nanoparticles were first anchored on the CNTs via controlled hydrolysis of Co(OAc)<sub>2</sub> (Figure S1) and then the oxide was converted to the corresponding phosphide via a solid/gas-phase reaction with PH<sub>3</sub>.<sup>28</sup> The CNTs are used as a support for the nanoparticles in order to facilitate good size control and uniform dispersion of the nanoparticles as well as to enhance electron conduction during electrochemical reactions. The scanning electron microscopy (SEM) images reveal that the CoP-CNT composite material possesses a well-defined morphology with 10-20 nm sized nanoparticles uniformly covering the CNT surface (Figure 1a, S2a). The natural CoP nanoparticles, having been stored under ambient conditions for several days, gain a partially oxidized surface, as evidenced by a Co 2p3/2 component at 781.1 eV and a P 2p doublets at 133.6/134.5 eV in the corresponding X-ray photoelectron spectroscopy (XPS) spectra (Figure 1b, c). This surface oxidation phenomenon is consistent with the literature on cobalt and other transition metal phosphide nanomaterials.<sup>29-31</sup> The oxidized CoP surface can be reduced by a thermal treatment at 500 °C in an Ar/H<sub>2</sub> atmosphere (Figure 1d). The resulting nanoparticles (CoP-R), which exhibit a comparable size distribution (Figure 1e, S2b) and the identical crystal structure (Figure 1f) as the original CoP nanoparticles, possess a fully reduced surface (Figure 1b, c)

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**Figure 1.** (a) SEM image of CoP nanoparticles supported on CNTs. (b) Co  $2p_{3/2}$  and (c) P 2p XPS spectra of CoP and CoP-R nanoparticles supported on CNTs. (d) Schematic illustration of the removal of the surface oxidation layer on CoP nanoparticles through thermochemical reduction to render CoP-R nanoparticles. (e) SEM image of CoP-R nanoparticles supported on CNTs. (f) XRD patterns of CoP and CoP-R nanoparticles supported on CNTs.

High-resolution transmission electron microscopy (HRTEM) further reveals the attachment of both CoP and CoP-R nanoparticles to CNTs as well as the lattice fringes corresponding to the (002) crystallographic planes of the CoP crystal structure (Figure 2a, b). Despite the identical bulk structures, the CoP and CoP-R nanoparticles show different surface structures under the scanning transmission electron microscopy (STEM) mode recorded with a high-angle annular dark-field (HAADF) detector. A core-shell-like structure with a lower-contrast outer layer corresponding to the surface oxidation region is observed for the CoP nanoparticles (Figure 2c), whereas the CoP-R nanoparticles show no obvious surface layer (Figure 2d). Consistently, a much higher O content is found in the CoP-CNT than that in the CoP-R-CNT material by energy dispersive X-ray spectroscopy (EDS) (Figure S3). EDS mapping reveals that the O atoms accumulate on the surface of the CoP nanoparticles (Figure 2e). In contrast, the CoP-R nanoparticles are almost free of O atoms on their surface, with the majority of the O signals contributed by the CNTs (Figure 2f).



**Figure 2.** (a, b) HRTEM, (c, d) STEM-HAADF images, and (e, f) EDS elemental distribution maps of (a, c, e) CoP and (b, d, f) CoP-R nanoparticles supported on CNTs.

We first assessed the LPS-confining capabilities of the natural and reduced CoP nanoparticles. The natural CoP nanoparticles with an oxidized surface exhibit a strong affinity for LPS (Figure 3a). The contribution from the CNT support can be eliminated since the CNTs themselves do not adsorb LPS. In striking contrast, the CoP-R with a reduced surface do not adsorb LPS (Figure 3a). Additional control experiments show that freshly synthesized CoP nanoparticles do not adsorb LPS (Figure S4a), whereas re-oxidized CoP-R nanoparticles can strongly adsorb LPS (Figure S4b), unambiguously correlating the LPS adsorbing capability with the oxidized surface. We then assembled symmetric cells comprising two identical CoP-CNT or CoP-R-CNT electrodes and a 0.4 M Li<sub>2</sub>S<sub>6</sub>-1,3dioxolane/dimethoxyethane (DOL/DME, 1:1 v/v) solution as the electrolyte to probe the electrochemical conversion of LPS at the electrode/electrolyte interface. Under identical measuring conditions, it is clearly observed that the cyclic voltammograms (CVs) of the CoP-CNT cell shows the highest current which reflects the fastest redox conversion of LPS on the electrode surface. The fast electrochemical reaction on the oxidized CoP surface is a result of both the high surface coverage of LPS and the low charge transfer resistance at the interface (Figure 3d). The former is verified by the LPS adsorption experiments, and the latter is confirmed by electrochemical impedance spectroscopy (EIS) measurements (Figure 3c).



Figure 3. (a) Results of LPS (5 mM  $Li_2S_6$ -DOL/DME solution) adsorption experiments with CNTs and CoP and CoP-R nanoparticles supported on CNTs. (b) CVs at the scan rate of 10 mV/s and

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(c) EIS spectra in the frequency range of 50 mHz to 200 kHz of symmetric cells containing a 0.4 M  $Li_2S_6$ -DOL/DME solution as the electrolyte and CNTs, CoP-CNT or CoP-R-CNT as the electrodes. (d) Schematic illustration of LPS adsorption and conversion behavior on the natural vs. reduced CoP surfaces.

To elucidate the chemical interactions between surfaceoxidized CoP and LPS, we performed XPS measurements for both the CoP and CoP-R nanoparticles after they were soaked in a LPS solution. The XPS studies were performed using free-standing nanoparticles without CNT supports (Figure S5). in order to avoid any interference from the CNTs. Both the Co 2p<sub>3/2</sub> and P 2p spectra of the natural CoP nanoparticles manifest notable features of oxidized Co and P species (Figure 4a, c). After the nanoparticles interacting with LPS, the intensity of the Co-O component in the Co  $2p_{3/2}$  spectrum greatly reduces while that of the Co-P/S component increases concomitantly (Figure 4a).<sup>32-33</sup> We attribute these spectral changes to the formation of Co-S bonding between the Co atom in the surface oxidation layer of the CoP nanoparticles and the S atom in the LPS. This is consistent with the observed growth of the component at 161.5 eV in the S 2p spectrum, which can be assigned to terminal S-Co bonding (Figure 4e).<sup>34-36</sup> The P 2p spectrum shows a minor decrease in the P-O component and a minor increase in the P-Co component, suggesting a slight reduction of the oxidized P species on the surface (Figure 4c), likely induced by the LPS. No binding energy shift is observed for the O 1s spectrum after the nanoparticles interacting with LPS (Figure S6). In contrast, the surface of the CoP-R nanoparticles with reduced Co and P species shows no discernable spectral changes in either the  $Co2p_{3/2}$  or P 2p XPS spectra after the nanoparticles are allowed to fully interact with LPS (Figure 4b, d), indicating that the CoP-R surface is unable to bind LPS. Consistently, the corresponding S 2p and Li 1s spectra possess negligible intensity (Figure 4e, S7).

Taken together, the drastically different LPS binding and adsorption behaviors of the CoP and CoP-R nanoparticles are ascribed to their different surface structures. On the reduced CoP surface, the Co-P bonds are weakly polarized. As a result, neither the Co nor the P sites are capable of generating a strong binding force for the  $S^{\delta}$  or the Li<sup> $\delta^+$ </sup> in the LPS, respectively. However, the oxidized CoP surface is dominated by Co-O-P-like species. The highly electronegative O creates high-valence Co sites which can react with short-chain LPS species to form Co-S bonding and leave Li-O-P moieties on the surface (Figure 4f). Our control experiments reveal that the oxidized species on the CoP nanoparticle surface highly resemble those on a  $Co_3(PO_4)_2$  (CoPi) surface and bind LPS in a similar way (Figure S8, S9). Taking CoPi as a proxy for the oxidized CoP surface, our density functional theory (DFT) calculations support that the interactions between LPS and the reduced CoP surface are weak (Figure S10a, b) and that surface oxidation can significantly enhance LPS binding via strengthened Co-S interactions (Figure S10c, S11). The binding modes of LPS on CoP nanoparticles are distinct from those on metal oxides where Li-O interactions are dominant.<sup>24</sup>



**Figure 4.** (a, b) Co  $2p_{3/2}$ , (c, d) P 2p and (e) S 2p XPS spectra of (a, c) CoP and (b, d) CoP-R nanoparticles before and after interacting with Li<sub>2</sub>S<sub>6</sub>. (f) Proposed binding schemes of LPS on CoP and CoP-R surfaces.

Finally, we incorporate CoP and CoP-R nanoparticles in sulfur cathodes by depositing nanoparticle-coated CNTs onto pre-made sulfur electrodes, and compare their electrochemical performance in LSBs. We first verify that CoP remains electrochemically inert within the operating potential range of sulfur electrodes (Figure S12). The CVs of the two cells containing either the CoP or CoP-R nanoparticles show the typical two-stage discharging and one-stage charging behavior of a sulfur cathode (Figure 5a).<sup>6,9,37</sup> It is noted that the CVs of the CoP-R cell possess much broader current peaks and a larger voltage hysteresis than those of the CoP cell. The difference in overpotential is also reflected in the galvanostatic charging-discharging curves (Figure S13a). This is consistent with our finding in the symmetric cells that the electrochemical conver-

sion of LPS is faster on the oxidized than the reduced CoP surface. The CoP-containing electrode with 3 mg cm<sup>-2</sup> of sulfur retains a specific capacity of 835 mAh g<sup>-1</sup> after 200 cycles at the 1C rate (Figure 5b). The cycling gives an average capacity decay of ~0.018% per cycle, together with the Coulombic efficiency >99.8% (Figure S13b). The CoP-R-containing electrode has a comparable initial capacity which, however, fades quickly to 683 mAh g<sup>-1</sup> after 200 cycles. The Coulombic efficiency also decreases upon cycling and falls obviously below that of the CoP-containing cell (Figure S13b). In fact, the performance of the CoP-R-containing electrode is very close to the electrode without any nanoparticles added, meaning that the CoP-R nanoparticles do not confine LPS. This is also well reflected in the post-cycling imaging results where the CoP-

containing electrode maintains the original particulate morphology whereas the sulfur particles on the CoP-R-containing electrode have fused into a gel-like structure likely due to LPS diffusion during the cycling process (Figure S14). To demonstrate usefulness toward practical applications, we further increase the sulfur mass loading in the CoP-containing electrode to 7 mg cm<sup>-2</sup>. The resulting electrode can still be stably cycled for 200 times with a specific capacity of 790 mAh g<sup>-1</sup> and an areal capacity of 5.6 mAh cm<sup>-2</sup> (Figure 5c).



**Figure 5.** (a) CVs of S cathodes (measured against a Li metal anode) modified with CoP-CNT and CoP-R-CNT. (b) Cycling stability of S cathodes (S mass loading: 3 mg cm<sup>-2</sup>; rate: 1C) modified with CNT, CoP-CNT, and CoP-R-CNT. (c) Cycling performance of a high-capacity S cathode (S mass loading: 7 mg cm<sup>-2</sup>; rate: 0.2C) modified with CoP-CNT.

In addition to CoP, we find that other metal phosphide and chalcogenide materials including Ni<sub>2</sub>P, FeP, MoP, CoS and CoSe<sub>2</sub> nanoparticles, most of which have been reported for effectively confining LPS and improving sulfur cathode performance,<sup>9, 18, 25, 38</sup> all rely on a surface oxidation layer to chemically bind LPS (Figure S15-17). This discovery reveals that the surface oxidation-activated LPS binding mechanism is a general phenomenon and can explain the functions of many transition metal phosphides and chalcogenides in stabilizing sulfur cathodes, highlighting the critical importance of understanding the surface chemistry in LSBs.

In summary, we have discovered a new and general LPSbinding mechanism enabled by surface oxidation layers of transition metal phosphide and chalcogenide materials. As an example, surface oxidation of CoP nanoparticles activates the Co sites for strongly binding LPS via Co-S bonding. Based on CoP nanoparticles with the surface oxidation layer binding LPS and the inner core facilitating electron conduction, we realize stable-cycling and high-capacity sulfur cathodes.

## ASSOCIATED CONTENT

Supporting Information.

The Supporting Information including complete experimental details, additional X-ray diffraction, electron microscopic, electrochemical and spectroscopic analyses, and additional LPS adsorption results, is available free of charge via the internet at http://pubs.acs.org.

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#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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