# Mechanistic Insights into Surface Chemical Interactions between Lithium Polysulfides and Transition Metal Oxides

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**Supporting Information** 

**ABSTRACT:** The design and development of materials for electrochemical energy storage and conversion devices requires fundamental understanding of chemical interactions at electrode/ electrolyte interfaces. For Li–S batteries that hold the promise for outperforming the current generation of Li ion batteries, the interactions of lithium polysulfide (LPS) intermediates with the electrode surface strongly influence the efficiency and cycle life of the sulfur cathode. While metal oxides have been demonstrated to be useful in trapping LPS, the actual binding modes of LPS on 3d transition metal oxides and their dependence on the metal element identity across the periodic table remain poorly



understood. Here, we investigate the chemical interactions between LPS and oxides of Mn, Fe, Co, and Cu by combining X-ray photoelectron spectroscopy and density functional theory calculations. We find that Li–O interactions dominate LPS binding to the oxides  $(Mn_3O_4, Fe_2O_3, and Co_3O_4)$ , with increasing strength from Mn to Fe to Co. For  $Co_3O_4$ , LPS binding also involves metal–sulfur interactions. We also find that the metal oxides exhibit different binding preferences for different LPS, with  $Co_3O_4$  binding shorter-chain LPS more strongly than  $Mn_3O_4$ . In contrast to the other oxides, CuO undergoes intense reduction and dissolution reactions upon interaction with LPS. The reported findings are thus particularly relevant to the design of LPS/oxide interfaces for high-performance Li–S batteries.

# 1. INTRODUCTION

Large-scale applications for electric vehicles and smart grids demand high-performance electrochemical energy storage systems beyond traditional Li-ion batteries.<sup>1–3</sup> Lithium–sulfur (Li–S) batteries are promising candidates for next-generation energy storage due to their high specific energy (2600 Wh kg<sup>-1</sup>), nontoxicity, and abundant natural reserves of the elements.<sup>4,5</sup> However, successful implementation of Li–S batteries is still hampered by limitations of the various battery components. Major adverse factors on the cathode side include insufficient sulfur utilization, low Coulombic efficiency, and rapid capacity attenuation, all of which relate to dissolution, diffusion, and side reactions of the lithium polysulfide (LPS) intermediates (Li<sub>2</sub>S<sub>x</sub>,  $4 \le x \le 8$ ) generated in the charging and discharging processes.<sup>6–8</sup> To achieve high-capacity, high-efficiency, and stablecycling Li–S batteries, it is essential to ensure confinement of LPS on the cathode.

During the past decade, significant efforts have been made toward achieving confinement of LPS,<sup>9–14</sup> with the focus shifting from using porous carbonaceous materials as physical barriers to utilizing host materials with polar surfaces for chemically adsorbing LPS.<sup>15–24</sup> Among the materials explored, metal oxides, such as MnO<sub>2</sub>, Ti<sub>4</sub>O<sub>7</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>, NiFe<sub>2</sub>O<sub>4</sub>, etc., can provide effective binding sites for LPS, significantly enhancing cycling stability of sulfur cathodes.<sup>25–30</sup> LPS adsorption on individual metal oxides have been studied, such as V<sub>2</sub>O<sub>5</sub> predicted by

theoretical calculations to bind LPS via Li–O interactions,<sup>31</sup> and Ti<sub>4</sub>O<sub>7</sub> surface shown to trap LPS relying on Ti–S interactions.<sup>28</sup> Nazar et al. have established the principles of oxidative LPS binding, where LPS are oxidized to thiosulfates or polythionates on metal oxide surfaces such as NiOOH, MnO<sub>2</sub>, and CuO.<sup>26,32</sup> Despite significant progress toward understanding surface interactions between LPS and metal oxides, the actual binding modes of LPS molecules on oxides of 3d transition metals remain elusive, particularly when there are no redox reactions at the interface.

Here, we report a systematic study on chemical interactions of LPS with oxides of a series of 3d transition metals (Mn, Fe, Co, and Cu). Combining X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations, we find that binding of Li ions of the LPS to O ions of the oxides ( $Mn_3O_4$ , Fe<sub>2</sub>O<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub>) are dominant interactions. The strength of Li–O binding increases in the order Mn < Fe < Co. Strong metal–sulfur binding is observed only for LPS adsorption on Co<sub>3</sub>O<sub>4</sub>. Furthermore, we find that metal oxides exhibit different binding preferences for different LPS. Co<sub>3</sub>O<sub>4</sub> tends to bind shorter-chain LPS more strongly than  $Mn_3O_4$  does. Surprisingly, upon interaction with LPS, the surface layer of CuO is converted

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**Figure 1.** O 1s XPS spectra of (a)  $Mn_3O_4$ , (b)  $Fe_2O_3$ , and (c)  $Co_3O_4$  before and after interacting with  $Li_2S_6$ . (d) Areal ratio of the Li–O component to the metal–O component for the three oxides.

to Li<sub>2</sub>O with Cu leaching into the solution, likely via a thermodynamically favorable reduction and dissolution pathway.

# 2. RESULTS AND DISCUSSION

Metal oxides were synthesized by hydrolysis reactions in an ethanol/water (10/1, V/V) mixed solvent under solvothermal conditions at 160 °C, resulting in nanoparticles of 5–20 nm (Figure S1). X-ray diffraction (XRD) analysis reveals the corresponding material phases to be  $Mn_3O_4$ ,  $Fe_2O_3$ ,  $Co_3O_4$ , and CuO (Figure S2). The observed XRD peak broadening confirms the nanoparticulate nature of the materials.

These metal oxides have been reported to be effective in binding LPS and stabilizing Li–S batteries.<sup>33–35</sup> In order to study the interaction chemistry, metal oxide powders were drop-casted onto Al foil to prepare the samples. The resulting metal oxide films were then each immersed in a separate 0.01 M Li<sub>2</sub>S<sub>6</sub> solution for 24 h in an Ar-filled glovebox before they were transferred by a vacuum transfer vessel (Figure S3) into the XPS spectrometer for examining the chemical states of the metal oxide surfaces after interacting with LPS.

The O 1s core-level spectra of the metal oxides (Figure 1) show good agreement with earlier studies.<sup>36</sup> For instance, the O 1s spectrum of  $Mn_3O_4$  exhibits a major component at the binding energy (BE) of 529.38 eV corresponding to lattice O-Mn bonding, together with a smaller component at 530.34 eV indicating the presence of Mn–OH as well as defective sites on the surface (Figure 1a). $^{37-39}$  After interacting with LPS, the higher BE component is replaced by a new peak centered at 531.22 eV with an increased proportion (Figure 1a), indicating the formation of O-Li bonding configuration similar to those (BE at ~531 eV) of lithium compounds.  $^{40-42}$  Upon O–Li binding, the positively charged Li withdraws valence electrons from the negatively charged O, which reduces the screening effect on the inner O 1s core-level electrons, consequently leading to the increase in BE.<sup>43</sup> The lattice O–Mn peak shifts slightly to lower BE (Figure 1a), likely owing to the electron density increase in the surface layer induced by O-Li binding. Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>

show similar spectral changes after binding LPS (Figure 1b,c). Interestingly, it is observed that the three metal oxides demonstrate different capabilities in binding LPS via O–Li interactions. Judging from the areal ratios of the O–Li component to the O–metal component in the O 1s spectra after the metal oxides interacting with LPS, the strength of interaction with LPS increases following the order  $Mn_3O_4 < Fe_2O_3 < Co_3O_4$  (Figure 1d).

In addition to O-Li binding, transition metal oxides may also adsorb LPS via metal-sulfur interactions. To identify possible metal-S binding for LPS adsorbed on the metal oxides, we investigated the metal 2p XPS spectra. As shown in Figure 2a, the Mn 2p<sub>3/2</sub> spectrum of Mn<sub>3</sub>O<sub>4</sub> consists of two components at 640.61 and 642.05 eV, ascribed to Mn<sup>2+</sup> and Mn<sup>4+</sup> according to previous reports.<sup>44</sup> Upon interaction of Mn<sub>3</sub>O<sub>4</sub> with LPS, no obvious changes are observed for either component except for a slight shift of 0.15 eV to lower BE (Figure 2a,d), suggesting no intense chemical interactions between Mn and S. Fe<sub>2</sub>O<sub>3</sub> exhibits similar spectral changes after interacting with LPS, with the two multiplet-splitting Fe(III) peaks<sup>36</sup> shifting to lower BE by 0.16 eV (Figure 2b,d).  $Co_3O_4$ , however, exhibits a much more significant BE shift of 0.57 eV to the lower end (Figure 2c,d), likely due to strong binding between the positively charged Co and the partially negatively charged S. These results suggest increasing strength of metal-sulfur binding, following the order  $Mn_3O_4 < Fe_2O_3 < Co_3O_4$ . This trend, from Mn to Fe and Co, is qualitatively correlated with the increasing metal-sulfur bonding strength, as reflected by the decreasing solubility product constants  $(K_{sp})$  of the corresponding binary sulfides (Table S1).

Figure 2e shows the S 2p XPS spectra. The spectrum of a dried  $Li_2S_6$  solution features two doublet components centered at 161.32/162.40 and 162.86/164.04 eV, corresponding to the terminal S atoms ( $S_T$ ) directly bonded with Li and the bridging S atoms ( $S_B$ ) directly bonded with S.<sup>26</sup> The areal ratio of  $S_B$  to  $S_T$  is roughly consistent with the nominal formula  $Li_2S_6$ . LPS adsorbed on  $Mn_3O_4$  gives a similar spectrum as that of  $Li_2S_6$  in terms of binding energy and  $S_B/S_T$  ratio. LPS adsorbed on

Intensity (a.u)

720





Figure 2. Metal  $2p_{3/2}$  XPS spectra of (a)  $Mn_3O_4$ , (b)  $Fe_2O_3$ , and (c)  $Co_3O_4$  before and after interacting with  $Li_2S_6$ . (d) BE shift of the metal  $2p_{3/2}$ components after interacting with Li<sub>2</sub>S<sub>6</sub>. (e) S 2p XPS spectra of dried Li<sub>2</sub>S<sub>6</sub> solution and Li<sub>2</sub>S<sub>6</sub> adsorbed on metal oxide surfaces.



Figure 3. (a) Schematic illustration of the CuO film after interacting with  $Li_2S_6$ . (b) Cu  $2p_{3/2}$  and (c) O 1s XPS spectra of CuO before and after interacting with  $Li_2S_6$ . The blue curve in (b) is a Cu  $2p_{3/2}$  spectrum of the CuO- $Li_2S_6$  sample with the surface layer peeled off manually. (d) S 2p XPS spectra of Li<sub>2</sub>S<sub>6</sub> and Li<sub>2</sub>S<sub>6</sub> adsorbed on the CuO film.

 $Fe_2O_3$  manifests a more decreased  $S_B/S_T$  ratio (~1:1) than  $Li_2S_{6'}$ attributed to stronger affinity for shorter-chain LPS. Following the trend, an even lower  $S_B/S_T$  ratio is observed for LPS adsorbed on Co<sub>3</sub>O<sub>4</sub>.

Interestingly, we find that CuO behaves strikingly differently from the other three metal oxides. The Cu  $2p_{3/2}$  XPS spectrum of CuO shows a major component centered at 933.53 eV and shakeup satellite features in the 940–945 eV range (Figure 3b),

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**Figure 4.** DFT optimized binding geometries and binding energies (BEs) of  $\text{Li}_2S_x$  (x = 2-6) on (a)  $\text{Mn}_3\text{O}_4(001)$  and (b)  $\text{Co}_3\text{O}_4(100)$  surfaces. (c) RBEs of  $\text{Li}_2S_x$  on  $\text{Mn}_3\text{O}_4(001)$  and  $\text{Co}_3\text{O}_4(100)$  surfaces. The light green, red, yellow, purple, and blue balls represent Li, O, S, Mn, and Co atoms, respectively.

characteristic of Cu(II).<sup>45</sup> However, after interacting with LPS, no Cu signals were detected by XPS (Figure 3b), indicating that the surface layer of the CuO film has been dissolved by the LPS solution, as verified by XPS detection of Cu-containing species in the dried solution (Figure S4). The O 1s core level spectrum shows only one peak around 532 eV (Figure 3c) ascribed to lithium oxide.<sup>42,46</sup> The S 2p spectrum is similar to that of pure  $\text{Li}_2\text{S}_6$  (Figure 3d), implying a lack of strong chemical binding to the surface. Cu signal could be detected by XPS after the surface layer of the film was peeled off. The recorded Cu  $2p_{3/2}$  spectrum features a peak at 932.23 eV without evident satellite peaks (Figure 3b), alluding to Cu (I) species.<sup>45</sup> With these results, we propose the following sequence of chemical reactions leading to the observed layered structure illustrated in Figure 3a:

$$\begin{aligned} & 6\mathrm{CuO}(\mathrm{s}) + 3\mathrm{Li}_2\mathrm{S}_6(\mathrm{sol}) \to 3\mathrm{Cu}_2\mathrm{O}(\mathrm{s}) + \mathrm{Li}_2\mathrm{S}_2\mathrm{O}_3(\mathrm{sol}) \\ & + 2\mathrm{Li}_2\mathrm{S}_8(\mathrm{sol}) \quad \Delta G = -25.5 \ \mathrm{kcal/mol} \end{aligned} \tag{1}$$

$$Cu_2O(s) + 4Li_2S_2O_3(sol) \rightarrow 2Li_3Cu(S_2O_3)_2(sol)$$
$$+ Li_2O(s) \quad \Delta G = -33.1 \text{ kcal/mol}$$

CuO is first reduced to Cu<sub>2</sub>O by Li<sub>2</sub>S<sub>6</sub>, forming thiosulfate species  $(S_2O_3^{2-})$ . A similar reaction has been previously reported in the literature.<sup>32</sup> Cu<sub>2</sub>O further reacts with Li<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to form a soluble Cu(I)–thiosulfate complex and an insoluble Li<sub>2</sub>O layer on the surface. Gibbs free energies of the two reactions are calculated to be significantly negative (–25.5 and –33.1 kcal/mol, respectively), verifying thermodynamic feasibility of the proposed reactions.

DFT calculations, using the Vienna *ab initio* Simulation Package (VASP),<sup>47–50</sup> provide valuable insights into the interactions between LPS and metal oxide surfaces. We use  $\text{Li}_2\text{S}_x$ (x = 2-6) as model LPS compounds and study their adsorption on the Mn<sub>3</sub>O<sub>4</sub>(001) and Co<sub>3</sub>O<sub>4</sub>(100) surfaces. The optimized structures with  $Li_2S_x$  binding to the metal oxide surfaces are shown in Figure 4.

The strength of interactions between  $Li_2S_x$  and metal oxide surfaces is quantified by the BE, defined as the energy difference between a metal oxide- $Li_2S_x$  complex and the corresponding isolated state. More negative BE indicates stronger interactions. We find that Co<sub>3</sub>O<sub>4</sub> binds Li<sub>2</sub>S<sub>6</sub> much more strongly than  $Mn_3O_4$ , as indicated by the much more negative BE of  $Li_2S_6$  to  $Co_3O_4$  (-3.79 eV) than that to  $Mn_3O_4$  (-1.84 eV). For  $Li_2S_6$ adsorbed on  $Mn_3O_4$ , the Mn-S bond distances are 2.4 and 2.5 Å, suggesting relatively weak metal-sulfur interactions. The bond distances between Li and O, however, are much smaller (2.0 Å), indicating that the Li-O binding is the dominant interaction. Li<sub>2</sub>S<sub>6</sub> adsorbed on Co<sub>3</sub>O<sub>4</sub> has significantly reduced metalsulfur (2.3 Å) and Li-O (1.9 Å) bond distances compared to the Mn<sub>3</sub>O<sub>4</sub> case, consistent with the XPS results, suggesting strengthened metal-sulfur and Li-O binding from Mn<sub>3</sub>O<sub>4</sub> to Co<sub>3</sub>O<sub>4</sub>. In fact, Figure 4 shows that for all the LPS considered in our calculations, the BEs on  $Co_3O_4(100)$  surface are much more negative than the corresponding BEs on  $Mn_3O_4(001)$ , indicating that Co<sub>3</sub>O<sub>4</sub> generally binds LPS much more strongly.

Considering that the Li<sub>2</sub>S<sub>6</sub> solution has all the other LPS,<sup>6,51</sup> we further studied the energy changes of the reactions for LPS generation from Li<sub>2</sub>S<sub>6</sub>: Li<sub>2</sub>S<sub>6</sub>  $\rightarrow$  Li<sub>2</sub>S<sub>x</sub> +  $\frac{6-x}{8}$ S<sub>8</sub> for x = 2-5. The calculated energy changes are 1.58, 0.58, 0.74, and 1.37 eV, for Li<sub>2</sub>S<sub>5</sub>, Li<sub>2</sub>S<sub>4</sub>, Li<sub>2</sub>S<sub>3</sub>, and Li<sub>2</sub>S<sub>2</sub>, respectively. The results suggest that Li<sub>2</sub>S<sub>6</sub> is the most stable LPS, while the other LPS are energetically disfavored. Next, we use relative BE (RBE) to evaluate the adsorption preference of different LPS (in a Li<sub>2</sub>S<sub>6</sub> solution) on metal oxides. The RBE is defined as the sum of the BE of a LPS and the energy cost to generate it from Li<sub>2</sub>S<sub>6</sub>. The RBE for Li<sub>2</sub>S<sub>6</sub>, Li<sub>2</sub>S<sub>5</sub>, Li<sub>2</sub>S<sub>4</sub>, Li<sub>2</sub>S<sub>3</sub>, and Li<sub>2</sub>S<sub>2</sub> on the Mn<sub>3</sub>O<sub>4</sub>(001) surface are -1.84, -1.77, -1.66, -1.09, and -1.22 eV, respectively, while those on the Co<sub>3</sub>O<sub>4</sub>(100) surface are -3.79, -4.70, -3.50,

(2)

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-4.70, and -3.63 eV, respectively. The results clearly indicate that the  $Mn_3O_4$  surface prefers to adsorb longer-chain LPS, while the  $Co_3O_4$  surface favors shorter-chain LPS, which agrees well with our experimental XPS observation showing that the LPS adsorbed on  $Co_3O_4$  has a lower  $S_B/S_T$  ratio than that on  $Mn_3O_4$ .

# 3. CONCLUSION

In summary, we have examined the nature of chemical interactions between LPS, an important class of intermediates in Li–S batteries, and 3d transition metal oxides, using XPS analyses and DFT calculations. Substantial Li–O binding is identified for LPS adsorbed on oxides of Mn, Fe, and Co. The strength of the interaction increases with increasing atomic number of the transition metal. Furthermore, we find that metal–sulfur interactions are significant for Co<sub>3</sub>O<sub>4</sub> while negligible for Mn<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>. For CuO, intense chemical reactions of Cu reduction and dissolution take place upon interacting with LPS. These findings thus elucidate critical chemical interactions and processes at LPS/oxide interfaces that should be particularly valuable to guide the design of materials for high-performance Li–S batteries.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b04170.

Experimental details, computational methods, and additional characterization (PDF)

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#### Notes

The authors declare no competing financial interest.

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