Supporting Information


Tuning Transition Metal Oxide–Sulfur Interactions for Long Life Lithium Sulfur Batteries: The “Goldilocks” Principle

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Supporting Information for:
Tuning transition metal oxide-sulfur interactions for long life lithium sulfur batteries: the ‘Goldilocks’ principle

Xiao Liang,1 Chun Yuen Kwok,1 Fernanda Lodi-Marzano,2 Quan Pang,1 Marine Cuisinier,1 He Huang,1 Connor J. Hart,1 Diane Houtarde,1 Kavish Kaup,1 Heino Sommer,2 Torsten Brezesinski,2 Jürgen Janek2 and Linda F. Nazar1,*

1University of Waterloo, Department of Chemistry and the Waterloo Institute of Nanotechnology, 200 University Ave., Waterloo, Ontario N2L 3G1, Canada
2Battery and Electrochemistry Laboratory, Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
Figure S1. CV profiles of the metal oxides: (a) Co$_3$O$_4$; (b) NiO; (c) Cu$_2$O; (d) CoO; (e) TiO$_2$; (f) Ti$_4$O$_7$; (g) V$_2$O$_3$; (h) MnO$_2$; (i) CuO; (j) VO$_2$; (k) NiOOH; (l) V$_2$O$_5$. The colors of the CV profiles refer to (grey) no redox; (green) redox to thiosulfate; (red) redox to thiosulfate and sulfate. CV tests were conducted with a scan rate of 0.05 mV·s$^{-1}$. All of the redox potentials were measured from the intersection of the first reduction peak on the cathodic sweep with the x-axis except for CoO and V$_2$O$_3$ which exhibit a higher oxide on the surface owing to atmospheric oxidation; here the 2$^{nd}$ reduction peak was used as a measure of the value of the bulk.
Metal oxides with a redox potential too low to form thiosulfate

1. Iron (III) oxide

Fe$_2$O$_3$ is reported to have a low redox potential versus Li/Li$^+$ (< 1.0 V), and is widely studied as an anode material for Li-ion batteries.$^{[1]}$ No changes were detected in the Fe 2p core spectrum after contact with LiPSs (Figure S2a, b). The S 2p spectrum for the Fe$_2$O$_3$-LiPSs composite also contains the same sulfur species compared to that of pristine LiPSs (Figure S2c). Therefore, Fe$_2$O$_3$ is redox inactive towards LiPSs.

![Fe 2p XPS core spectra](image)

**Figure S2.** Fe 2p XPS core spectra of (a) commercial Fe$_2$O$_3$ and (b) Fe$_2$O$_3$-Li$_2$S$_4$ and (c) S 2p XPS core spectrum of Fe$_2$O$_3$-Li$_2$S$_4$. 

\[ \text{Fe}^{3+} \]

\[ \text{S}^{2-} \]

\[ \text{S}_8^{0} \]

Intensity (a.u.)

Binding energy (eV)

Intensity (a.u.)

Binding energy (eV)
2. Cobalt (II) oxide

Due to the surface oxidation of CoO to Co$_2$O$_3$, the XPS spectrum of CoO shows both Co$^{3+}$ and Co$^{2+}$ (Figure S3a). No valence change occurred for the metal upon contacting these cobalt oxides with LiPSs, which is further confirmed by analysis of the S 2p core spectra (Figure S3b,c) where peaks only correlate to the ‘bridging’ and ‘terminal’ S environment of pristine Li$_2$S$_4$.

![Figure S3](image_url)

**Figure S3.** Co 2p XPS core spectra of (a) commercial CoO and (b) CoO-Li$_2$S$_4$ and (c) S 2p XPS core spectrum of CoO-Li$_2$S$_4$. 
3. Copper (I) oxide

Surface analysis of Cu$_2$O (Figure S4a) contains a dominant peak from Cu$^{1+}$ and a minor peak that is fitted with a multiplet from Cu$^{2+}$, indicating the surface was slightly oxidized. The presence of the minor satellite peak area from 942-948 eV is also evidence of the presence of CuO on the surface. Upon contact with LiPSs, the higher valence state of copper is reduced to Cu$^{+1}$ as confirmed by the disappearance of the peaks in the Cu 2p core spectrum (Figure S4b). The weak thiosulfate signal in the S 2p core spectrum for Cu$_2$O-LiPSs originates from the reduction of the surface CuO (Figure S4c).

![Figure S4. Cu 2p XPS core spectra of (a) commercial Cu$_2$O and (b) Cu$_2$O-Li$_2$S$_4$; S 2p XPS core spectrum of (c) Cu$_2$O-Li$_2$S$_4$.]
4. **Nickel (II) oxide**

XPS data of commercial NiO (Figure S5a) was fit using a multiplet that contains only a single Ni (II) valence state.[2] Given that NiO represents the lowest oxidation state possible for nickel, it is reasonable to assume that on contact with LiPSs (Figure S5b) nickel cannot be further reduced. This was confirmed by the S 2p spectrum (Figure S5c) where the major components simply correlate to the binding energy of LiPSs.

![Figure S5. Ni 2p XPS core spectra of (a) commercial NiO and (b) NiO-Li$_2$S$_4$; S 2p XPS core spectrum of (c) NiO-Li$_2$S$_4$.](image_url)
Figure S6. EDAX analysis of VO$_x$-graphene. (a) SEM image; elemental mapping of (b) O and (c) V. (d) TGA curve of pristine VO$_x$-graphene in air, showing there is ~25 wt. % graphene in the composite.
Figure S7. (a) SEM and (b) HRTEM image of V$_2$O$_3$-graphene, showing V$_2$O$_3$ nanocrystals, with index to the (113) lattice planes of the oxide; XPS spectra of the V$_2$O$_3$-graphene and solids recovered from vanadium oxide-Li$_2$S$_4$ suspensions, (c) V 2p spectrum of V$_2$O$_3$, (b) V 2p spectrum of V$_2$O$_3$-Li$_2$S$_4$ and (c) S 2p spectrum of V$_2$O$_3$-Li$_2$S$_4$. 
Figure S8. N$_2$ absorption/desorption isotherms of VO$_x$-graphene and Co$_3$O$_4$-graphene from which the BET surface area was calculated.
Figure S9. XPS spectra of the Co$_3$O$_4$-graphene and solids recovered from Co$_3$O$_4$-Li$_2$S$_4$ suspensions, (c) Co 2p spectrum of Co$_3$O$_4$, (b) Co 2p spectrum of Co$_3$O$_4$-Li$_2$S$_4$ and (c) S 2p spectrum of Co$_3$O$_4$-Li$_2$S$_4$. 
Figure S10. SEM images (a-b) of (a) S/V$_2$O$_5$-graphene and (b) S/VO$_2$-graphene, (c) S/Co$_3$O$_4$-graphene; (d) TGA profiles of the S/V$_2$O$_5$-graphene, S/VO$_2$-graphene and S/Co$_3$O$_4$-graphene, showing a sulfur content of 75 wt%. The scale bar is 1 µm.
Figure S11. EDAX analysis of S/VO$_2$-graphene. (a) SEM image; elemental mapping of (b) S; (c) O; and (d) V. The scale bar is 2 $\mu$m.
Figure S12. Charge/discharge profiles at C/2 for S/Co$_3$O$_4$-graphene (blue), S/VO$_2$-graphene (black) and S/V$_2$O$_5$-graphene (red) electrodes. The solid lines are the 2nd cycle and the dashed lines are the 200th cycle.
Figure S13. (a) XRD pattern and (b) Raman spectrum obtained on V$_2$O$_5$ hollow spheres. The diffraction peaks and Raman bands can be indexed to the orthorhombic phase in space group *Pmmn* (JCPDS card no. 41-1426). Note that only the most intense peaks are indexed in panel (a).
References