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Promoting Sulfur Adsorption using Surface Cu Sites in Metal-Organic Frameworks for Lithium Sulfur Batteries

Avery Baumann,¹ Gabrielle E. Aversa,¹ Anindya Roy,² Michael Falk,^{2,4,5} Nicholas Bedford,³ V. Sara Thoi^{1*}

¹Department of Chemistry, Johns Hopkins University, Baltimore, MD

²Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD

³Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH

⁴Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD

⁵Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD

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 Table S4. Numeric results of total sulfur content determined by TGA from at least 4 individual syntheses of CuBTC@S with varying particle sizes



Figure S1. Calculated S-MOF DFT structures and interaction energies (graph reproduced from Figure 1)



Figure S2. EXAFS k-space for 5.9 mm CuBTC at various S loading



Figure S3. EXAFS Fitting for a) 5.9 μ m CuBTC and at varied S loading: b) 0.5 S:MOF, c) 1.0 S:MOF, and d) 1.5 S:MOF



Figure S4. Representative TGA curves of (a) elemental sulfur and (b) CuBTC, and assignments (reproduced from Figure 3a). The TGA of CuBTC is featureless between 110-300 °C, while the sulfur TGA shows only the sulfur degradation below 300 °C. The features assigned in Figure 3 for Physi-S and Chemi-S are assigned using this information and previous identification of physi- and chemisorbed water at elevated temperatures.^{1,2}



Figure S5. PXRD patterns of (a) as-synthesized CuBTC, and (b) CuBTC@S. The MOF powder pattern remains unchanged upon sulfur loading.



Figure S6. FT-IR spectra of (a) as-synthesized CuBTC, and (b) CuBTC@S. Characteristic stretches at 1372, 1446 and 730 cm⁻¹ correspond to v(C=O), v(C-O), and v(Cu-O) signals, respectively.^{3,4}



Figure S7. Raman spectra show CuBTC@S has clear shifts in the Cu-Cu (*) and the Cu-L ($^{\circ}$) regions from the unloaded CuBTC. The major peaks at 150, 220 and 240 cm⁻¹ in CuBTC@S correspond to S-S bonds, while the peak at 230 cm⁻¹ is attributed to DCM in CuBTC.⁵



Figure S8. Particle size distributions as measured from scanning electron micrographs using Image J, a free image processing software. Distributions are shown for (a) $5.9 \mu m$, (b) $1.6 \mu m$, and (c) $0.16 \mu m$ CuBTC.



Figure S9. Raman spectra of as-synthesized CuBTC. The Cu-Cu and C=C bands of the paddlewheel and BTC linker are denoted by (*) and (\circ) respectively. The increasing relative intensity of Cu-Cu to C=C bands at 168 and 1,006 cm⁻¹, respectively, as a function of decreasing particle size suggests higher paddlewheel densities in 0.16 µm CuBTC.



Figure S10. Compositional differences as a function of particle size are shown using TGA and EDS Smaller particles have a higher Cu:C ratio, suggesting higher Cu content for the 0.16 and 1.6 µm CuBTC particles than in the 5.9 µm particles.



Figure S11. Atomic absorption spectrum shows increased Cu content with decreasing particle size.



Figure S12. (a) XANES and (b) EXAFS for 5.9 μ m, 1.6 μ m, and 0.16 μ m CuBTC and CuBTC@S at 1.5 S:MOF loading. (c) EXAFS *k*-space for 0.2 and 1.6 μ m CuBTC at 1.5 S:MOF loading



Figure S13. EXAFS Fitting for (a) 1.6 μ m CuBTC; (b) 1.6 μ m CuBTC@S at a 1.5 S:MOF loading; (c) 0.6 μ m CuBTC; and (d) 0.16 μ m CuBTC@S at a 1.5 S:MOF loading



Figure S14. Aliquots taken at (a) 8 h and (b) 12 h during the open-cell polysulfide leaching experiments for CuBTC@S and S/C were measured using UV-Vis absorbance spectroscopy.



Figure S15. (a) PXRD and (b) FT-IR of activated 5.9 μ m CuBTC soaked in Li₂S₄ solution. CuBTC shows stability in the polysulfide solution and retains its bulk structure characteristics.



Figure S16. Cyclic voltammetry for CuBTC@S and S/C coin cells, showing the (a) first scan, and (b) fifth scan at a scan rate of 0.1 mV/s between 2.9 - 1.6 V.



Figure S17. Galvanostatic charge and discharge curves for (a) 0.16 μ m CuBTC@S, (b) 1.6 μ m CuBTC@S, and (c) 5.9 μ m CuBTC@S. The C-rate is C/10 for cycles 1-20 and C/5 for cycles 21-100. The potential window is 2.9 – 1.6 V versus Li/Li⁺.



Figure S18. Average capacity retention for CuBTC@S coin cells after 100 cycles.

Table S1. EXAFS fitting results for 5.9 μ m CuBTC@S samples at various S-loading showing (a) coordination number (CN) and (b) the nearest neighbor distances (NND).

(a)				
Sample	Cu-O CN	Cu-Cu CN	Cu-O _w CN	Cu-S CN
5.9 μm CuBTC	4.26 ± 0.35	0.89 ± 0.13	1.1 ± 0.29	-
5.9 μm CuBTC 0.5 S	3.43 ± 0.54	1.1 ± 0.15	0.46 ± 0.23	0.49 ± 0.14
5.9 μm CuBTC 1.0 S	2.83 ± 0.85	0.95 ± 0.18	0.44 ± 0.13	0.58 ± 0.11
5.9 μm CuBTC 1.5 S	2.76 ± 0.66	0.72 ± 0.08	0.38 ± 0.11	0.62 ± 0.08
(b)				
(b) Sample	Cu-O NND (Å)	Cu-Cu NND (Å)	Cu-O _w NND (Å)	Cu-S NND (Å)
(b) Sample 5.9 mm CuBTC	Cu-O NND (Å) 1.92 ± 0.01	Cu-Cu NND (Å) 2.55 ± 0.03	Cu-O_w NND (Å) 2.29 ± 0.02	Cu-S NND (Å) -
(b) Sample 5.9 mm CuBTC 5.9 mm CuBTC 0.5 S	Cu-O NND (Å) 1.92 ± 0.01 1.94 ± 0.03	Cu-Cu NND (Å) 2.55 ± 0.03 2.56 ± 0.03	Cu-O_w NND (Å) 2.29 ± 0.02 2.29 ± 0.01	Cu-S NND (Å) - 2.21 ± 0.01
(b) Sample 5.9 mm CuBTC 5.9 mm CuBTC 0.5 S 5.9 mm CuBTC 1.0 S	Cu-O NND (Å) 1.92 ± 0.01 1.94 ± 0.03 1.97 ± 0.04	Cu-Cu NND (Å) 2.55 ± 0.03 2.56 ± 0.03 2.61 ± 0.05	Cu-O_w NND (Å) 2.29 ± 0.02 2.29 ± 0.01 2.25 ± 0.02	Cu-S NND (Å) - 2.21 ± 0.01 2.28 ± 0.03

Table S2. Relative Raman intensity (I) of Cu-Cu and C=C bands showing compositional differences in paddlewheel (Cu-Cu) to BTC (C=C) as a function of particle size

CuBTC Sample	I _{Cu-Cu} (168 cm⁻¹)	I _{C=C} (1006 cm ⁻¹)	I _{Cu-Cu} /I _{C=C}
0.16 μm	14.12	13.68	1.032
1.6 μm	10.85	12.96	0.837
5.9 μm	17.70	24.51	0.722

Table S3. EXAFS fitting results for various particle size samples at a 1.5 sulfur loading showing (a) coordination number (CN) and (b) nearest neaighbor distance (NND)

(a)				
Sample	Cu-O CN	Cu-Cu CN	Cu-O _w CN	Cu-S CN
0.16 μm CuBTC	2.83 ± 0.45	0.67 ± 0.11	0.9 ± 0.05	-
1.6 μm CuBTC	2.54 ± 0.34	0.59 ± 0.16	0.87 ± 0.18	-
5.9 μm CuBTC	4.26 ± 0.35	0.89 ± 0.13	1.1 ± 0.29	-
0.16 μm CuBTC@S	3.10 ± 0.72	0.42 ± 0.07	0.41 ± 0.11	0.67 ± 0.09
1.6 μm CuBTC@S	2.65 ± 0.44	0.51 ± 0.11	0.46 ± 0.06	0.60 ± 0.04
5.9 μm CuBTC@S	2.76 ± 0.66	0.72 ± 0.08	0.38 ± 0.11	0.62 ± 0.08
(b)				
(b) Sample	Cu-O NND (Å)	Cu-Cu NND (Å)	Cu-O _w NND (Å)	Cu-S NND (Å)
(b) Sample 0.16 μm CuBTC	Cu-O NND (Å) 1.93 ± 0.02	Cu-Cu NND (Å) 2.46 ± 0.05	Cu-O_w NND (Å) 2.33 ± 0.05	Cu-S NND (Å)
(b) Sample 0.16 μm CuBTC 1.6 μm CuBTC	Cu-O NND (Å) 1.93 ± 0.02 1.95 ± 0.01	Cu-Cu NND (Å) 2.46 ± 0.05 2.47 ± 0.03	Cu-O_w NND (Å) 2.33 ± 0.05 2.24 ± 0.02	Cu-S NND (Å) - -
(b) Sample 0.16 μm CuBTC 1.6 μm CuBTC 5.9 μm CuBTC	Cu-O NND (Å) 1.93 ± 0.02 1.95 ± 0.01 1.92 ± 0.01	Cu-Cu NND (Å) 2.46 ± 0.05 2.47 ± 0.03 2.55 ± 0.03	Cu-O _w NND (Å) 2.33 \pm 0.05 2.24 \pm 0.02 2.29 \pm 0.02	Cu-S NND (Å) - - -
(b) Sample 0.16 μm CuBTC 1.6 μm CuBTC 5.9 μm CuBTC 0.16 μm CuBTC@S	Cu-O NND (Å) 1.93 ± 0.02 1.95 ± 0.01 1.92 ± 0.01 1.95 ± 0.01	Cu-Cu NND (Å) 2.46 ± 0.05 2.47 ± 0.03 2.55 ± 0.03 2.59 ± 0.02	Cu-O _w NND (Å) 2.33 \pm 0.05 2.24 \pm 0.02 2.29 \pm 0.02 2.29 \pm 0.04	Cu-S NND (Å) - - 2.31 ± 0.02
(b) Sample 0.16 μm CuBTC 1.6 μm CuBTC 5.9 μm CuBTC@S 1.6 μm CuBTC@S	Cu-O NND (Å) 1.93 ± 0.02 1.95 ± 0.01 1.92 ± 0.01 1.95 ± 0.01 1.96 ± 0.03	Cu-Cu NND (Å) 2.46 ± 0.05 2.47 ± 0.03 2.55 ± 0.03 2.59 ± 0.02 2.61 ± 0.05	Cu-O _w NND (Å) 2.33 \pm 0.05 2.24 \pm 0.02 2.29 \pm 0.02 2.29 \pm 0.04 2.26 \pm 0.01	Cu-S NND (Å) - - 2.31 ± 0.02 2.30 ± 0.02
(b) Sample 0.16 μm CuBTC 1.6 μm CuBTC 5.9 μm CuBTC@S 1.6 μm CuBTC@S 5.9 μm CuBTC@S	Cu-O NND (Å) 1.93 ± 0.02 1.95 ± 0.01 1.92 ± 0.01 1.95 ± 0.01 1.96 ± 0.03 1.95 ± 0.01	Cu-Cu NND (Å) 2.46 ± 0.05 2.47 ± 0.03 2.55 ± 0.03 2.59 ± 0.02 2.61 ± 0.05 2.59 ± 0.02	Cu-O _w NND (Å) 2.33 ± 0.05 2.24 ± 0.02 2.29 ± 0.02 2.29 ± 0.04 2.26 ± 0.01 2.29 ± 0.04	Cu-S NND (Å) - - 2.31 ± 0.02 2.30 ± 0.02 2.31 ± 0.02

Table S4	. Numeric resu	lts of total s	sulfur conte	ent from a	t least 4	4 individual	l syntheses	of CuBTC@	S with
varying p	article sizes.								

Sample	Total S (Weight %)
0.16 μm CuBTC@S	66.8 ± 3.5
1.6 μm CuBTC@S	63.5 ± 4.4
5.9 μm CuBTC@S	65.2 ± 5.4

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