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Three-dimensional Covalent Organic Frameworks as Host Materials for Lithium-Sulfur Batteries

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Electronic Supplementary Information

Abstract Two reported three-dimensional covalent organic frameworks (3D-COFs), COF-300 and COF-301, which have hierarchical porous structures and large pore volumes, were synthesized and employed as host materials for lithium-sulfur batteries. Owing to possessing excellent porosities as well as abundant hydroxyl groups in the pore walls, COF-301 can not only trap lithium polysulfides (PSs) via physical adsorption inside the pores, but also capture PSs by chemical interactions to relieve the shuttle effect. Interestingly, it is the first time that 3D-COFs were utilized as host materials for lithium-sulfur batteries as well as hydroxyl groups were introduced into COFs for improving the battery performance. As a result, COF-301@S as cathode material could reserve the capacity of 411.6 mA·h·g⁻¹ after 500 cycles with only 0.081% fading per cycle at 0.5 C, exhibiting better battery performance compared with COF-300@S. This study not only expands the applications of 3D-COFs but also provides a new route for designing lithium-sulfur batteries.

Keywords Three-dimensional covalent organic framework; Host material; Lithium-sulfur battery; Hydroxyl group; Chemical interaction

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INTRODUCTION

Lithium-sulfur (Li-S) batteries have drawn tremendous attentions in recent years by virtue of their desirable capacity, high energy density, low cost as well as environmental friendliness of active sulfur.^[1–3] However, despite their tremendous potential, several drawbacks have impeded Li-S batteries for practical application. The major one is the shuttle effect of lithium polysulfides (PSs), which may result in a lower content of active sulfur and poor cycling performance.^[4–7] Numerous efforts have been attempted to avert the shuttle phenomenon, and one of the effective methods is to confine sulfur or soluble PSs into host materials for improving the availability of sulfur and alleviating dissolution or migration of PSs during the long cycling.^[8,9] For enhancing the performance of Li-S batteries, the host materials should satisfy the following features: (1)

hierarchical porous structures and suitable pore sizes for impregnation of active sulfur, for example, micropores for restricting the PSs from migrating to electrolyte, and mesopores for promoting the infiltration rate of PSs from electrolyte to sulfur; (2) large pore volumes for addressing sulfur expansion during cycling and loading higher amount of active materials; and (3) abundant functional groups (oxygenated functional groups) or surface modification (heteroatom doping) for enhancing the chemical interactions between hosts and PSs. According to the above mentioned features, porous materials can be regarded as ideal materials for hosts.^[3] Among the reported porous materials,^[10] metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have been attractive candidates because their structures and pores can be precisely controlled and designed by connecting different building blocks at molecular level. Especially owing to the good thermal stability, light element component, and low density of COFs,^[11–15] several two-dimensional COFs (2D-COFs) have been employed and reported as host materials recently.^[16–27] These works take advantages of 2D layered structures supplying well-organized pores for infiltration of sulfur, 1D channels offering routes for charge and ion motion across the frameworks, and trapping the PSs via physical/chemical interactions to improve

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the battery performance. Compared with the layered structure 2D-COFs, three-dimensional COFs (3D-COFs) are connected through specific building blocks (tetrahedral or other stereo) to form extended network structures, which have higher surface area, sufficient open sites, and good stability.^[28–33] Although utilizing 3D-COFs as host materials has not been reported yet, we consider that 3D-COFs are potential candidates for host materials on the basis of their favorable features (micro/mesoporous structure, large pore volume, high surface area, and adjustable skeleton). Interestingly, as reported, the oxygen-containing groups (particularly hydroxyl) can act as nucleation sites to obtain well-dispersed sulfur through hydrogen bond as well as can undergo redox reaction with PSs to relieve the shuttle effect.^[34–36] Therefore, introducing hydroxyl groups into COFs' pore walls may be a good approach for improving the battery performance.

Here, we synthesised two well-known 3D-COFs (COF-300 and COF-301) as host materials for Li-S batteries. COF-300 and COF-301 possess hierarchical porous structure, large pore volume, low density, and good thermal/chemical stability, which would be beneficial to constraining the PSs by physical or chemical interactions (hydroxyl groups in COF-301). The physical encapsulation of sulfur and chemical interactions with PSs are in favor of inhibiting the shuttle effect and improving the performance of Li-S batteries.

EXPERIMENTAL

Synthesis of COF-300

COF-300 was synthesized according to the reported literature.^[28] Terephthalaldehyde (TA) (24 mg, 0.179 mmol) and tetra(4-anilyl)methane (TAM) (40 mg, 0.105 mmol) were dissolved in anhydrous 1,4-dioxane (2 mL) and aqueous acetic acid (3 mol·L⁻¹, 0.4 mL) in a 10 mL glass tube. The tube was flash frozen at 77 K, evacuated, and flame-sealed. The reaction proceeded under 120 °C for 3 days. Then a light yellow solid was collected by centrifugation and washed with tetrahydrofuran (THF) and acetone for four times. The resulting powder was dried in a vacuum oven at 100 °C overnight to obtain a light yellow solid.

Synthesis of COF-301

COF-301 was synthesized according to reported literature.^[37] A 10 mL glass tube was charged with TAM (40 mg, 0.105 mmol) and 2,5-dihydroxyterephthalaldehyde (DHTA) (30.8 mg, 0.185 mmol) in a mixture of *o*-dichlorobenzene/*N,N*-dimethylacetamide (*o*-DCB/DMAc, 0.29 mL/1.71 mL) and aqueous acetic acid (6 mol·L⁻¹, 0.4 mL). The tube was then evacuated and flame-sealed. The reaction proceeded under 120 °C for 3 days. Then a brown solid was collected by centrifugation and washed with THF and acetone. The resulting powder was dried in a vacuum oven at 100 °C overnight to obtain a vermilion solid.

Synthesis of COF-300@S and COF-301@S

COF-300@S and COF-301@S were prepared by using similar reported procedure.^[16] Taking COF-300@S as an example, COF-300 (40 mg) and elemental sulfur (60 mg) were mixed in a glass tube (weight ratio COF/S = 4/6), and then the tube was degassed and flame-sealed. The mixture was heated at 155 °C for 12 h. After cooling down, the product COF-300@S was obtained.

Electrochemical Measurements

The cathode slurry was prepared by mixing 60 wt% COF-300@S (or COF-301@S), 30 wt% acetylene black, and 10 wt% poly(tetrafluoroethylene) (PVDF) in *N*-methyl-2-pyrrolidone (NMP) solution. Then the slurry was coated onto the surface of aluminum foil and dried at 60 °C for 12 h. The content of active sulfur was 1.5 mg·cm⁻². Lithium sheet was used as the counter electrode, polypropylene membranes as the separator, and the electrolyte was 1.0 mol·L⁻¹ lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, V:V) with 1 wt% LiNO₃ additive. The coin cells were assembled in an argon-filled glove box, and the diameter of cathode, separator, and anode was 11, 16, and 14 mm, respectively. The galvanostatic discharge/charge experiments were performed at a voltage interval of 1.7–2.8 V (versus Li⁺/Li) on a LAND CT2005A testing system. The specific capacity was calculated on the basis of the active sulfur material. The current density set for tests was referred to the mass of sulfur in the cathode and was varied from 0.2 C to 1 C, where 1 C = 1675 mA·h·g⁻¹. CV measurement was conducted on a CHI660E electrochemical workstation with a scan rate of 0.1 mV·s⁻¹ in the potential range of 1.7–2.8 V. EIS results were collected on a CHI660E electrochemical workstation.

Assembly of Li₂S₆ Symmetric Cells and Measurements

The electrodes for symmetric cells were fabricated without the presence of elemental sulfur. The 3D-COFs/acetylene black/PVDF electrodes were used as identical working and counter electrode with 30 μL electrolyte (0.5 mol·L⁻¹ Li₂S₆ and 1 mol·L⁻¹ LiTFSI dissolved in DOL/DME (1/1, V:V)). Cyclic voltammetry (CV) measurements of the symmetric cells were performed at a scan rate of 50 mV·s⁻¹ between –1.5 and 1.5 V.

RESULTS AND DISCUSSION

Structural Characterization

Herein, we synthesised COF-300 and COF-301 based on the reported literatures by condensation reactions of tetrahedral TAM and linear building blocks (TA for COF-300, and DHTA for COF-301) under solvothermal conditions (Fig. 1a).^[28,30,37] The characteristic bands corresponding to the –C=N– stretching vibration are shown at around 1620 cm⁻¹ in Fourier transform infrared (FTIR) spectra of these COFs, and solid-state ¹³C-NMR spectra show that the signals ascribed to imine carbons appear at 160 ppm, indicating the successful formation of imine bonds in both COF-300 and COF-301 (Figs. S1 and S2 in the electronic supplementary information, ESI). The crystallinity of these COFs was examined by powder X-ray diffraction (PXRD) measurement. As shown in Fig. 1(b), COF-300 and COF-301 display the strongest peak at 6.44° and 8.42°, respectively, which are consistent with the reported literatures.^[28,30,37] After impregnating sulfur into host 3D-COFs, no obvious crystalline peaks for sulfur can be observed in PXRD patterns of COF-300@S and COF-301@S, indicating that sulfur was dispersed uniformly inside the nanoporous spaces of COFs.

Nitrogen sorption isotherm measurements were employed to estimate the porosity of COFs under 77 K (Fig. 1c, Fig. S3 in ESI). The sorption curves of COF-300 and COF-301 displayed a typical type I and IV sorption isotherms, revealing that COFs possess both micro- and mesoporous porous structures. The

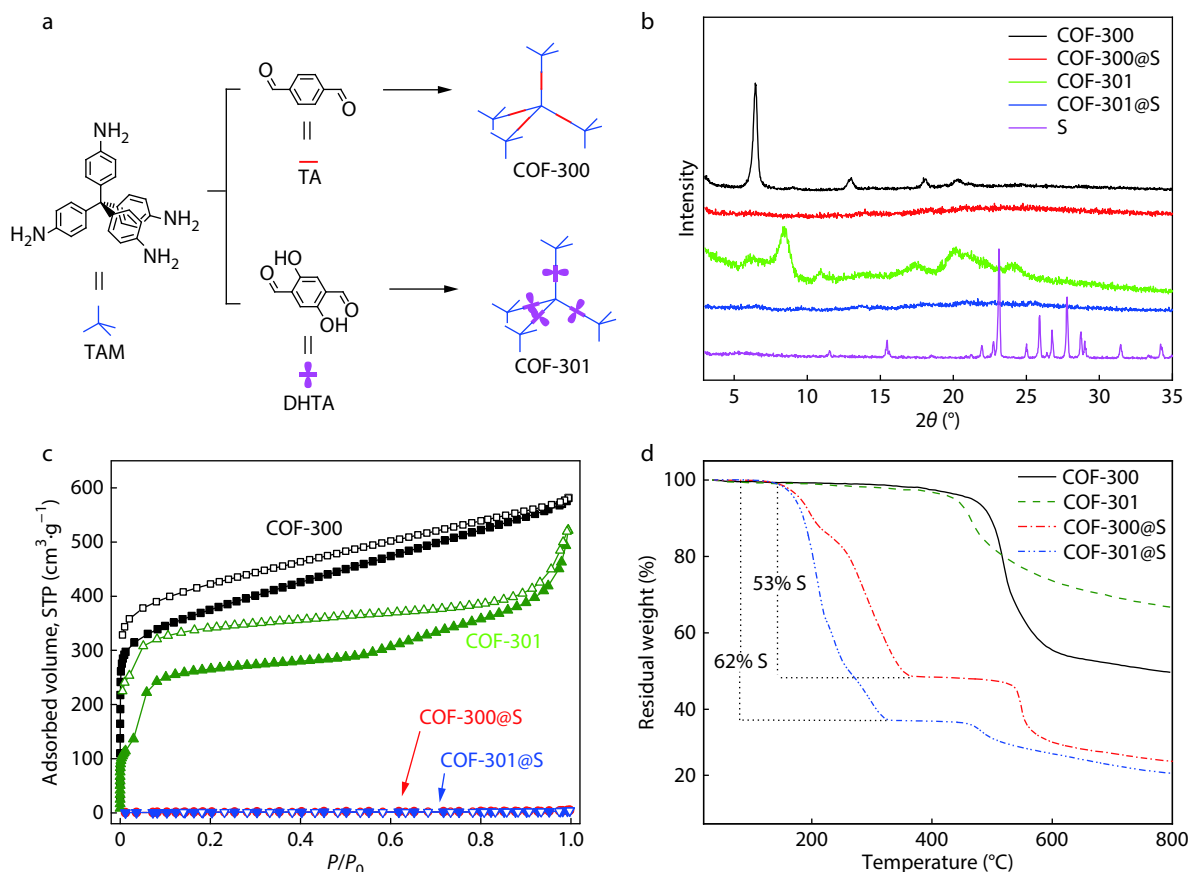


Fig. 1 (a) Synthesis of 3D-COFs. (b) PXRD patterns of 3D-COFs, 3D-COFs@S, and S. (c) Nitrogen sorption isotherm curves of 3D-COFs, and 3D-COFs@S measured under 77 K. (d) TGA curves of 3D-COFs and 3D-COFs@S.

Brunauer-Emmett-Teller (BET) specific surface area (SSA) values and pore volumes were calculated to be 1360 m²·g⁻¹ and 0.88 cm³·g⁻¹ for COF-300, as well as 1040 m²·g⁻¹ and 0.72 cm³·g⁻¹ for COF-301. By contrast, the BET SSA and pore volume of COFs@S decreased sharply after impregnation of sulfur with only 7 m²·g⁻¹ and 0.011 cm³·g⁻¹ for COF-300@S, 4 m²·g⁻¹ and 0.008 cm³·g⁻¹ for COF-301@S, suggesting that sulfur nearly filled up porous structures of the COFs. The content of sulfur in COFs@S confirmed by thermal gravimetric analysis (TGA) was 53% and 62% for COF-300@S and COF-301@S, respectively (Fig. 1d). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to investigate the morphology of COFs and COFs@S (Figs. S4 and S5 in ESI). By observing the SEM images of COF-300 and COF-300@S, their morphology changed little before and after impregnation of sulfur, which means no bulk sulfur in COF-300@S and sulfur was successfully encapsulated in COF-300 (similar results can also be observed in images of COF-301 and COF-301@S, Figs. S4 and S5 in ESI).

Battery Performance

The electrochemical performances were investigated by assembled coin cells, which were fabricated by employing metallic Li as anode and COF-300@S (or COF-301@S) as cathode materials. In the cathodic scan, the cyclic voltammetry (CV) curves of Li/COF-300@S cell display reduction peaks at 1.97 and 2.26 V, which are typical features of sulfur cathodes and caused

by the reduction reactions of sulfur to form the PSs and Li₂S/Li₂S₂ (Fig. 2a).^[38] Meanwhile, a broad oxidation peak can be observed at 2.42 V in the anodic scan, which implies the oxidation reactions of Li₂S transforming into Li₂S_x ($X = 2, 4, 6$ and 8 ; $X \geq 4$, highly soluble species) and sulfur occurred. In the CV curves of Li/COF-301@S cell, similar oxidation peak can be detected, and lower voltage gaps between reduction and oxidation peaks compared with Li/COF-300@S cell indicate that COF-301@S had a lower polarization.^[39] According to the electrochemical impedance spectroscopy (EIS) plots (Fig. 2b, Fig. S6 and Table S1 in ESI), the fresh Li/COF@S cell exhibited relatively low resistance (57 Ω for Li/COF-300@S cell and 27 Ω for Li/COF-301@S cell).

The galvanostatic discharge/charge measurements were employed to evaluate the rate performance of the cells at the current density of 0.2, 0.5, and 1 C (1 C = 1675 mA·h·g⁻¹) (Fig. 2c). The specific capacities of Li/COF-300@S cell were 922.1, 642.2, and 603.4 mA·h·g⁻¹ corresponding to the current density at 0.2, 0.5, and 1 C, respectively. Interestingly, when the current was returned from 1 C back to 0.2 C, the capacity of 640.5 mA·h·g⁻¹ was obtained. As a comparison, the Li/COF-301@S cell exhibited higher specific capacities of 940.0, 782.7 and 627.9 mA·h·g⁻¹ at 0.2, 0.5, and 1 C, respectively, and regained capacities of 796.5 mA·h·g⁻¹ when current went back to 0.2 C. Obviously, Li/COF-301@S cell exhibited a better rate performance and higher capacities compared with Li/COF-

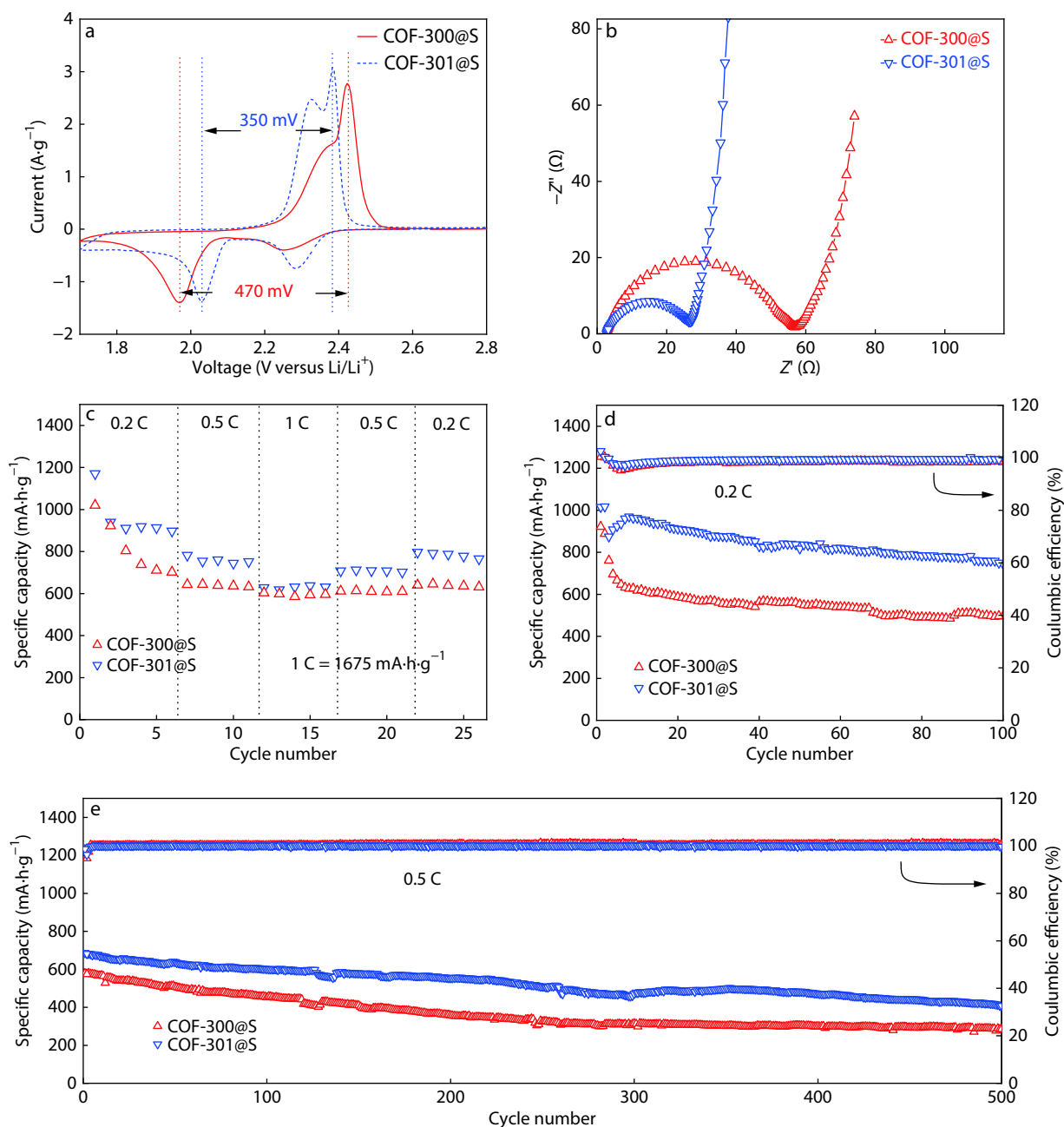


Fig. 2 (a) CV curves of Li/COF@S cells at a scan rate of 0.1 mV·S⁻¹. (b) EIS curves of Li/COF@S cells. (c) Rate performances of Li/COF@S cells at different current densities. (d) Cycling performances of Li/COF@S cells at 0.2 C for 200 cycles. (e) Long cycling performances of Li/COF@S cells at 0.5 C for 500 cycles.

300@S cell, maybe due to its higher sulfur loading and having abundant hydroxyl groups in the pore walls that possess strong interaction with lithium polysulfides and could alleviate the shuttle effect.^[34,35] In the charge/discharge curves of Li/COF-300@S and Li/COF-301@S at different current densities (Fig. S7 in ESI), a short platform at about 2.4 V and a long one at 2.1 V can be observed in discharge profiles, implying sulfur had experienced two oxidation reaction stages to form the long chain PSs, and these results coincide with the CV peaks as mentioned before. The enlarging of voltage gaps between charge and discharge profiles with current density

increase maybe due to the polarization of the cell.

The cycling stabilities of the Li/COF@S cells were measured to evaluate the cell performance of COF-300@S and COF-301@S cathodes. The content of sulfur in the cathode electrodes of COF-301@S was calculated to be 1.5 mg·cm⁻², and Li/COF-301@S exhibited the first discharge capacity of 874.0 mA·h·g⁻¹ at 0.2 C. As shown in Fig. 2(d), the discharge capacity gradually decreased to 751.2 mA·h·g⁻¹ after 100 cycles with 0.14% drop per cycle, and the Coulombic efficiency was close to 100%. In the meanwhile, COF-300@S exhibited a lower discharge capacity of 761.2 mA·h·g⁻¹ at 0.2 C,

and the capacity quickly faded to $487.4 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100 cycles (0.36% decay per cycle). These results reveal that oxygenated functional groups (hydroxyl groups) in the pore walls of COFs would be in favour of enhancing the battery performance. Furthermore, long cycling performance of Li/COF@S cells was studied at a higher current density at 0.5 C (Fig. 2e). Li/COF-301@S exhibited the initial discharge capacity of $690.9 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, and after 500 cycles the capacity reserved $411.6 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ with only 0.081% decay per cycle. By contrast, Li/COF-300@S showed a lower initial capacity and remained at $289.7 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 500 cycles. COF-301@S exhibited a relatively good battery performance compared with COF-300@S and most of reported 2D-COF based Li-S batteries (Table S2 in ESI).^[16,17,18,19,22,24,26] It may be owing to the special structure of COF-301 that can trap PSs *via* physical adsorption inside the pores, capture PSs by chemical interactions through hydrogen bonding, and experience redox reaction with soluble long PSs to form the insoluble short PSs for relieving the shuttle effect.^[36]

Shuttle effect is the inevitable process in damping the performance of Li-S batteries.^[4,5] To deeply understand the advantages of 3D-COFs host materials in adsorption of PSs, the interactions between COF-300 (or COF-301) and Li_2S_6 in DME solutions were tested to evaluate their PSs adsorption capabilities (Fig. S8 in ESI). After 1 h, COF-300 with only physical ad-

sorption of PSs had little effect on Li_2S_6 /DME solutions since the color was shallowed slightly. Nevertheless, COF-301 could absorb a majority of Li_2S_6 as the solution's color faded obviously to light yellow. The different adsorption capabilities of COF-300 and COF-301 toward PSs reveal a strong interactions between Li_2S_6 and COF-301 *via* chemical affinity. After washing the COFs through centrifugation processes, FTIR measurements were employed to examine the differences in the structures of 3D-COFs after adsorption of Li_2S_6 (Fig. 3a in ESI). The bands of —C=N— stretching vibration at 1620 cm^{-1} remain well after adsorption, indicating the structures of COFs were reserved during the dissolving of Li_2S_6 . Interestingly, the characteristic band at 1370 cm^{-1} ascribed to —OH bending vibration in COF-301 disappears after adsorption (sample COF-301@ Li_2S_6), suggesting chemical reactions occurred between COF-301 and Li_2S_6 .

To further confirm that the COF-300 and COF-301 can contribute to redox kinetic reaction with PSs conversion in batteries, the CV methods were utilized for testing Li_2S_6 and Li_2S_6 -free symmetric cells in the voltage windows from -1.5 V to 1.5 V .^[40] As shown in Fig. 3(b), for the symmetric cell without Li_2S_6 , the current densities of both COF-300@S and COF-301@S are low. For symmetric cell with Li_2S_6 , the current densities of COF-301@S are much larger with obvious redox peaks compared with COF-300@S, indicating that COF-301

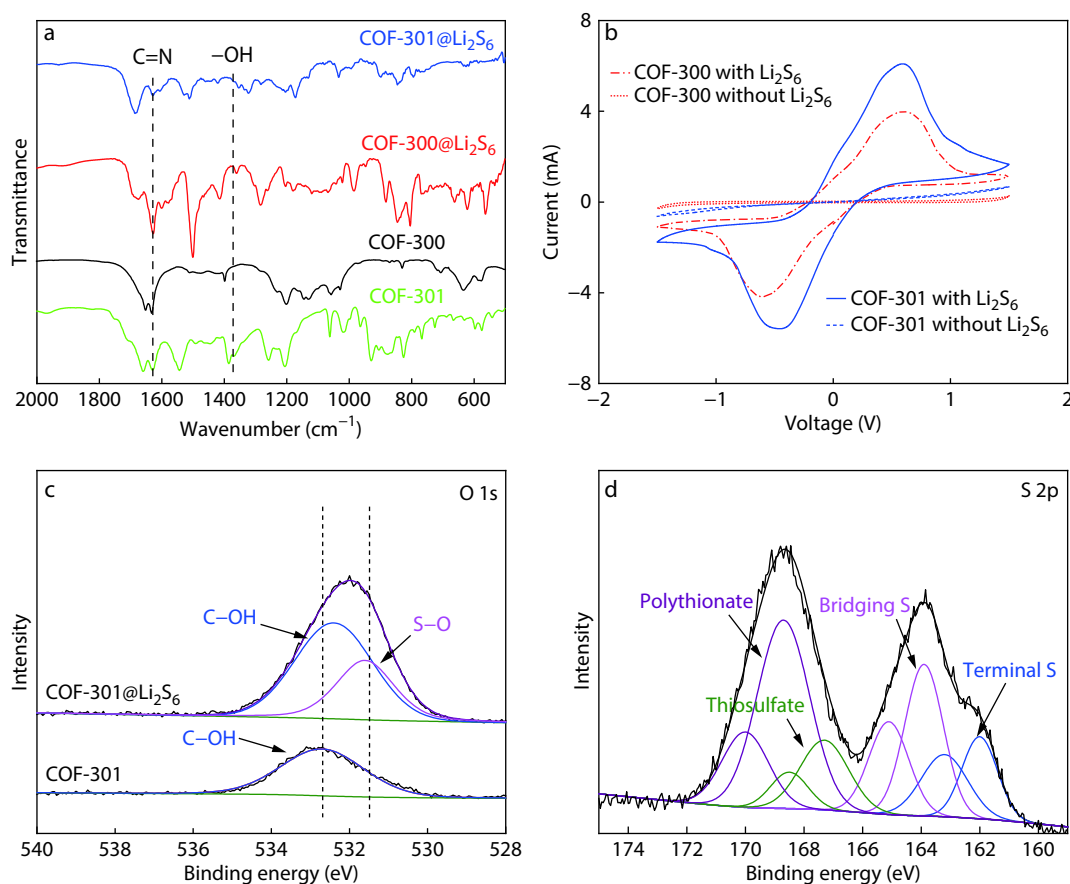


Fig. 3 (a) FTIR spectra of 3D-COFs and 3D-COFs@S. (b) CV curves of symmetric cells with identical electrodes of COF-300 and COF-301 electrodes in electrolytes with/without Li_2S_6 at $50 \text{ mV}\cdot\text{s}^{-1}$. (c) O 1s XPS spectra of COF-301 and COF-301@ Li_2S_6 . (d) S 2p XPS spectrum of COF-301@ Li_2S_6 .

could interact well with PSs and improve the redox kinetic reaction for catalyzing the conversion of PSs.^[41,42] The chemical interactions between COF-301 and PSs were examined by X-ray photoelectron spectra (XPS) measurement. The O 1s XPS spectrum of COF-301 exhibits a binding energy peak at 532.7 eV, ascribed to carbon-oxygen bond with C—OH environment (Fig. 3C). After adsorption of Li_2S_6 solutions, this peak of COF-301@ Li_2S_6 negatively shifts to 532.3 eV, and a new binding energy peak emerges at 531.5 eV corresponding to S—O environment. The variations in XPS spectra show that sulfur and PSs can act as electron donors to offer the electrons to electron-defect oxygen atoms in the pore walls of COF-301, resulting in strong chemical interaction between COF-301 and PSs.^[43] The S 2p XPS spectrum of COF-301@ Li_2S_6 exhibits four sulfur environments. As shown in Fig. 3(d), terminal sulfur (162.0 eV) and bridging sulfur (163.9 eV) in Li_2S_6 can be observed. The peaks at 167.2 and 168.7 eV can be ascribed to the binding energies of thiosulfate and polythionate, respectively, and these two peaks are originated from the redox reaction between Li_2S_6 and hydroxyl groups. To further comprehend the interactions between 3D-COF host and highly soluble Li_2S_X species (Li_2S_4 , Li_2S_6 and Li_2S_8), density functional theory (DFT) calculations were utilized to evaluate the optimized structures and binding energy between the host materials and Li_2S_X species (Figs. S9, S10, and S11 in ESI). As shown in Fig. S11 (in ESI), the binding energies exhibit negative values, revealing a stable environment and spontaneous adsorption process between COF and Li_2S_X through the favorable interactions. The binding energies are in the range 227.46–323.24 $\text{kJ}\cdot\text{mol}^{-1}$ for COF-301/ Li_2S_X , and these values are much higher than those of COF-300/ Li_2S_X with the identical kind of Li_2S_X . Therefore, the DFT calculations show COF-301

as host possesses higher binding energy value, which can adsorb highly soluble Li_2S_X more effectively. In addition, the introduction of oxygenated functional groups into COFs can increase the active sites of the electrode, and the increase in hole-type charge carriers can improve electronic conductivity and inhibit the polysulfide shuttling effect, which is very important for enhancing the battery performance.^[44–46] Combining the DFT calculations and S 2p XPS spectrum results, the interactions between Li_2S_6 and hydroxyl groups can be supposed as follows.^[47] At first, in discharging process, hydroxyl groups can capture and convert the long-chain PSs to form the thiosulfate, and then thiosulfate can nucleophilically attack soluble Li_2S_X ($X \geq 4$) to form the mediator polythionate complexes. Finally, the thiosulfate anchors the soluble Li_2S_X ($X \geq 4$) to transform into insoluble Li_2S_X ($X = 1$ and 2) and remarkably relieve the shuttle effect (Fig. 4). The above results afford assertive evidence that COF-301 as host can strongly weaken the shuttle effect and is appropriate for building high performance Li-S batteries.

CONCLUSIONS

We employed the 3D-COFs as the host materials for constructing high performance Li-S batteries with good long cycling performance (Li/COF-301@S can maintain 411.6 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ capacity after 500 cycles at 0.5 C with only 0.081% decay per cycle). COF-301 with well-defined porous structure and oxygenated functional groups (hydroxyl groups) in the pore walls could constrain the PSs by physical and chemical interactions. As a contrast, COF-300 that only had physical interactions with PSs exhibited unsatisfactory battery performance. This work not only expands the application fields of 3D-COFs, but also pro-

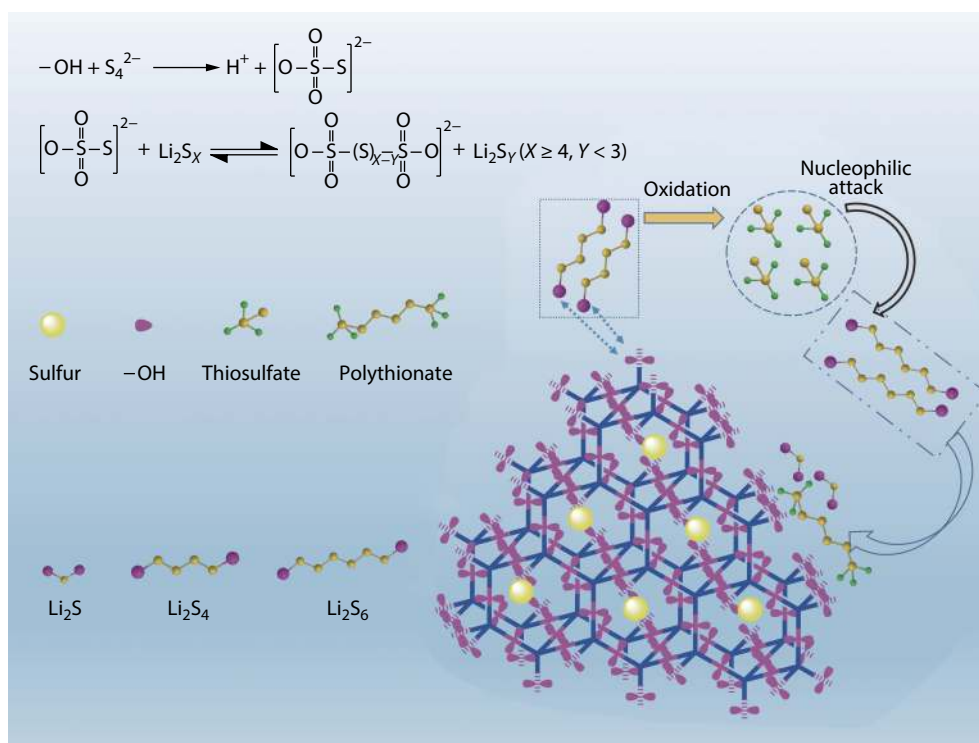


Fig. 4 Schematic illustration of the interactions between polysulfides and hydroxyl groups.

vides a new strategy that introducing appropriate oxygenated functional groups into COFs pore walls can constrain PSs and relieve the shuttle phenomenon effectively, which may open a new way to construct high performance Li-S batteries.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2384-z>.

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REFERENCES

- Manthiram, A.; Fu, Y.; Su, Y. S. Challenges and prospects of lithium-sulfur batteries. *Acc. Chem. Res.* **2013**, *46*, 1125–1134.
- Manthiram, A.; Fu, Y.; Chung, S. H.; Zu, C.; Su, Y. S. Rechargeable lithium-sulfur batteries. *Chem. Rev.* **2014**, *114*, 11751–11787.
- Yin, Y. X.; Xin, S.; Guo, Y. G.; Wan, L. J. Lithium-sulfur batteries: electrochemistry, materials, and prospects. *Angew. Chem. Int. Ed.* **2013**, *52*, 13186–13200.
- Evers, S.; Nazar, L. F. New approaches for high energy density lithium-sulfur battery cathodes. *Acc. Chem. Res.* **2013**, *46*, 1135–1143.
- Fang, R.; Zhao, S.; Sun, Z.; Wang, D. W.; Cheng, H. M.; Li, F. More reliable lithium-sulfur batteries: status, solutions and prospects. *Adv. Mater.* **2017**, *29*, 1606823.
- Zhao, F.; Li, Y.; Feng, W. Recent advances in applying vulcanization/inverse vulcanization methods to achieve high-performance sulfurcontaining polymer cathode materials for Li-S batteries. *Small Methods* **2018**, *2*, 1800156.
- Han, J.; Li, Y.; Li, S.; Long, P.; Cao, C.; Cao, Y.; Wang, W.; Feng, Y.; Feng, W. A low cost ultra-microporous carbon scaffold with confined chain-like sulfur molecules as a superior cathode for lithium-sulfur batteries. *Sustainable Energy Fuels* **2018**, *2*, 2187–2196.
- Ji, X. L.; Lee, K. T.; Nazar, L. F. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat. Mater.* **2009**, *28*, 500–506.
- Yang, Y.; Zheng, G. Y.; Cui, Y. Nanostructured sulfur cathodes. *Chem. Soc. Rev.* **2013**, *42*, 3018–3032.
- Chen, Z.; Pan, H.; Zhong, H.; Xiao, Z.; Li, X.; Wang, R. Porous organic polymers for polysulfide trapping in lithium-sulfur batteries. *Adv. Funct. Mater.* **2018**, *28*, 1707597.
- Feng, X.; Ding, X.; Jiang, D. Covalent organic frameworks. *Chem. Soc. Rev.* **2012**, *41*, 6010–6022.
- Ding, S. Y.; Wang, W. Covalent organic frameworks (COFs): from design to applications. *Chem. Soc. Rev.* **2013**, *42*, 548–568.
- Segura, J. L.; Mancheño, M. J.; Zamora, F. Covalent organic frameworks based on schiff-base chemistry: synthesis, properties and potential applications. *Chem. Soc. Rev.* **2016**, *45*, 5635–5671.
- Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of covalent organic frameworks. *Acc. Chem. Res.* **2015**, *48*, 3053–3063.
- Jiang, J.; Zhao, Y.; Yaghi, O. M. Covalent chemistry beyond molecules. *J. Am. Chem. Soc.* **2016**, *138*, 3255–3265.
- Liao, H.; Ding, H.; Li, B.; Ai, X.; Wang, C. Covalent organic frameworks: potential host materials for sulfur impregnation in lithium-sulfur batteries. *J. Mater. Chem. A* **2014**, *2*, 8854–8858.
- Yang, X.; Dong, B.; Zhang, H.; Ge, R.; Gao, Y.; Zhang, H. Sulfur impregnated in a mesoporous covalent organic framework for high performance lithium-sulfur batteries. *RSC Adv.* **2015**, *5*, 86137–86143.
- Liao, H.; Wang, H.; Ding, H.; Meng, X.; Xu, H.; Wang, B.; Ai, X.; Wang, C. A 2D porous porphyrin-based covalent organic framework for sulfur storage in lithium-sulfur batteries. *J. Mater. Chem. A* **2016**, *4*, 7416–7421.
- Ghazi, Z. A.; Zhu, L.; Wang, H.; Naeem, A.; Khattak, A. M.; Liang, B.; Khan, N. A.; Wei, Z.; Li, L.; Tang, Z. Efficient polysulfide chemisorption in covalent organic frameworks for high-performance lithium-sulfur batteries. *Adv. Energy Mater.* **2016**, *6*, 1601250.
- Yoo, J. T.; Cho, S. J.; Jung, G. Y.; Kim, S. H.; Choi, K. H.; Kim, J. H.; Lee, C. K.; Kwak, S. K.; Lee, S. Y. COF-net on CNT-net as a molecularly designed, hierarchical porous chemical trap for polysulfides in lithium-sulfur batteries. *Nano Lett.* **2016**, *16*, 3292–3300.
- Jiang, C.; Tang, M.; Zhu, S.; Zhang, J.; Wu, Y.; Chen, Y.; Xia, C.; Wang, C.; Hu, W. Constructing universal ionic sieves via alignment of two-dimensional covalent organic frameworks (COFs). *Angew. Chem. Int. Ed.* **2018**, *57*, 16072–16076.
- Wang, D.-G. Li, N.; Hu, Y.; Wan, S.; Song, M.; Yu, G.; Jin, Y.; Wei, W.; Han, K.; Kuang, G. C.; Zhang, W. Highly fluoro-substituted covalent organic framework and its application in lithium-sulfur batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 42233–42240.
- Song, X.; Zhang, M.; Yao, M.; Hao, C.; Qiu, J. New insights into the anchoring mechanism of polysulfides inside nanoporous covalent organic frameworks for lithium-sulfur batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 43896–43903.
- Xiao, Z.; Li, L.; Tang, Y.; Cheng, Z.; Pan, H.; Tian, D.; Wang, R. Covalent organic frameworks with lithiophilic and sulfiphilic dual linkages for cooperative affinity to polysulfides in lithium-sulfur batteries. *Energy Storage Mater.* **2018**, *12*, 252–259.
- Meng, Y.; Lin, G.; Ding, H.; Liao, H.; Wang, C. Impregnation of sulfur into a 2D pyrene-based covalent organic framework for high-rate lithium-sulfur batteries. *J. Mater. Chem. A* **2018**, *6*, 17186–17191.
- Jiang, Q.; Li, Y.; Zhao, X.; Xiong, P.; Yu, X.; Xu, Y.; Chen, L. Inverse-Vulcanization of vinyl functionalized covalent organic frameworks as efficient cathode materials for Li-S Batteries. *J. Mater. Chem. A* **2018**, *6*, 17977–17981.
- Wang, J.; Si, L.; Wei, Q.; Hong, X.; Lin, L.; Li, X.; Chen, J.; Wen, P.; Cai, Y. An imine-linked covalent organic framework as the host material for sulfur loading in lithium-sulfur batteries. *J. Energy Chem.* **2019**, *28*, 54–60.
- Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klöck, C.; O’Keeffe, M.; Yaghi, O. M. A crystalline imine-linked 3-D porous covalent organic framework. *J. Am. Chem. Soc.* **2009**, *131*, 4570–4571.
- Zhang, Y.-B.; Su, J.; Furukawa, H.; Yun, Y.; Gándara, F.; Duong, A.; Zou, X.; Yaghi, O. M. Single-crystal structure of a covalent organic framework. *J. Am. Chem. Soc.* **2013**, *135*, 16336–16339.
- Pramudya, Y.; Mendoza-Cortes, J. L. Design principles for high H₂ storage using chelation of abundant transition metals in covalent organic frameworks for 0–700 bar at 298 K. *J. Am. Chem. Soc.* **2016**, *138*, 15204–15213.
- Lin, G.; Ding, H.; Chen, R.; Peng, Z.; Wang, B.; Wang, C. 3D porphyrin-based covalent organic frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 8705–8709.
- Li, H.; Pan, Q.; Ma, Y.; Guan, X.; Xue, M.; Fang, Q.; Yan, Y.; Valtchev, V.; Qiu, S. Three-dimensional covalent organic frameworks with

- dual linkages for bifunctional cascade catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 14783–14788.
- 33 Yan, S.; Guan, X.; Li, H.; Li, D.; Xue, M.; Yan, Y.; Valtchev, V.; Qiu, S.; Fang, Q. Three-dimensional salphen-based covalent organic frameworks as catalytic antioxidants. *J. Am. Chem. Soc.* **2019**, *141*, 2920–2924.
 - 34 Chen, M.; Wang, X.; Cai, S.; Ma, Z.; Song, P.; Fisher, A. C. Enhancing the performance of lithium-sulfur batteries by anchoring polar polymers on the surface of sulfur host materials. *J. Mater. Chem. A* **2016**, *4*, 16148–16156.
 - 35 Dive, A. M.; Song, M. K.; Banerjee, S. Physisorption mechanism of solvated polysulfide chains on graphene oxides with varied functional groups. *J. Phys. Chem. C* **2017**, *121*, 5089–5098.
 - 36 Ge, X.; Li, C.; Li, Z.; Yin, L. Tannic acid tuned metal-organic framework as a high-efficiency chemical anchor of polysulfide for lithium-sulfur batteries. *Electrochim. Acta* **2018**, *281*, 700–709.
 - 37 Li, Z.; Ding, X.; Feng, Y.; Feng, W.; Han, B. H. Structural and dimensional transformations between covalent organic frameworks via linker exchange. *Macromolecules* **2019**, *52*, 1257–1265.
 - 38 Han, K.; Liu, Z.; Shen, J.; Lin, Y.; Dai, F.; Ye, H. A free-standing and ultralong-life lithium-selenium battery cathode enabled by 3D mesoporous carbon/graphene hierarchical architecture. *Adv. Funct. Mater.* **2015**, *25*, 455–463.
 - 39 Xu, K.; Liu, X.; Liang, J.; Cai, J.; Zhang, K.; Lu, Y.; Wu, X.; Zhu, M.; Liu, Y.; Zhu, Y.; Wang, G.; Qan, Y. Manipulating the redox kinetics of Li-S chemistry by tellurium doping for improved Li-S batteries. *ACS Energy Lett.* **2018**, *3*, 420–427.
 - 40 Lin, H.; Yang, L.; Jiang, X.; Li, G.; Zhang, T.; Yao, Q.; Zheng, G. Y. W.; Lee, J. Y. Electrocatalysis of polysulfide conversion by sulfur-deficient MoS₂ nanoflakes for lithium-sulfur batteries. *Energy Environ. Sci.* **2017**, *10*, 1476–1486.
 - 41 Huang, S.; Lim, Y. V.; Zhang, X.; Wang, Y.; Zheng, Y.; Kong, D.; Ding, M.; Yang, S. A.; Yang, H. Y. Regulating the polysulfide redox conversion by iron phosphide nanocrystals for high-rate and ultrastable lithium-sulfur battery. *Nano Energy* **2018**, *51*, 340–348.
 - 42 Wang, S.; Liao, J.; Yang, X.; Liang, J.; Sun, Q.; Liang, J.; Zhao, F.; Koo, A.; Kong, F.; Yao, Y.; Gao, X.; Wu, M.; Yang, S. Z.; Li, R.; Sun, X. Designing a highly efficient polysulfide conversion catalyst with paramontroseite for high-performance and long-life lithium-sulfur batteries. *Nano Energy* **2019**, *59*, 230–240.
 - 43 Lang, X.; Hart, C.; Pang, Q.; Garsuch, A.; Weiss, T.; Nazar, L. F. A highly efficient polysulfide mediator for lithium-sulfur batteries. *Nat. Commun.* **2015**, *6*, 5682.
 - 44 Hou, T.; Xu, W.; Chen, X.; Peng, H.; Huang, J.; Zhang, Q. Lithium bond chemistry in lithium-sulfur batteries. *Angew. Chem. Int. Ed.* **2017**, *56*, 8178–8182.
 - 45 Chen, X.; Xu, Y.; Du, F.; Wang, Y. Covalent organic framework derived boron/oxygen codoped porous carbon on CNTs as an efficient sulfur host for lithium-sulfur batteries. *Small Methods* **2019**, *3*, 1900338.
 - 46 Li, B.; Peng, H.; Chen, X.; Zhang, S.; Xie, J.; Zhao, C.; Zhang, Q. Polysulfide electrocatalysis on framework porphyrin in high-capacity and high-stable lithium-sulfur batteries. *CCS Chem.* **2019**, *1*, 128–137.
 - 47 Liao, X.; Kwok, C. Y.; Lodi-Marzano, F.; Pang, Q.; Cuisinier, M.; Huang, H.; Hart, C. J.; Houtarde, D.; Kaup, P.; Sommer, H.; Brezesinski, T.; Janek, J.; Nazar, L. F. Tuning transition metal oxide-sulfur interactions for long life lithium-sulfur batteries: the “goldilocks” principle. *Adv. Energy Mater.* **2016**, *6*, 1501636.