**Understanding the Origin of Irreversible Capacity loss in Non-Carbonized Carbonate –
based Metal Organic Framework (MOF) Sulfur hosts for Lithium – Sulfur battery**

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4 **Abstract:**
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7 Li-Sulfur (Li-S) batteries are emergent next-generation energy storage devices due to their very
8 high specific energy density ($\sim 2567 \text{ Wh g}^{-1}$) but are limited by polysulfide dissolution issues. In
9 this work, chemically synthesized sulfur containing non-carbonized metal organic framework (S-
10 MOF) cathodes show initial specific capacities of 1476 mAh g^{-1} stabilizing at $\sim 609 \text{ mAh g}^{-1}$ with
11 almost no fade for over 200 cycles. Post-cycled separators of the S – MOF cathodes display
12 complete absence of polysulfides after cycle 1, 20 and 200. It was identified that the occurrence
13 of carbonate species in the MOF structure resulted in the formation of C-S bonded species
14 causing retention of polysulfide at the electrode surface ensuring long-term stability. However,
15 this observed capacity drop during the first 10 cycles is attributed to the oxidation of some of the
16 infiltrated sulfur by the MOF as determined by electrochemical and X-ray photoelectron
17 spectroscopy (XPS) analyses. Nevertheless, the negligible fade rate ($0.0014\% \text{ cycle}^{-1}$) and
18 complete prevention of polysulfide dissolution renders these cathodes most promising candidates
19 for Li-S batteries. Understanding of this transformation behavior in sulfur-containing MOF is
20 essential to engineer chemically-bonded host-structures capable of efficient polysulfide trapping,
21 a key pathway to establishing novel platforms for achieving high power Li – S batteries.
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44 **Key words:** Metal organic framework; Lithium-Sulfur; Polysulfide; Encapsulation
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1. Introduction:

In recent years, there is a near exponential increase in the demand for plug – in hybrid vehicles (PHEV) combined with the use of portable electronic devices, together providing the impetus for portable energy storage devices with greater output/mass or volume. Commercial Li – ion batteries since the first Li-ion battery introduced by Sony in 1990 based on lithiation chemistry are limited by a maximum theoretical capacity of $\sim 546 \text{ Wh kg}^{-1}$ [1] and are incapable of meeting this ever increasing demand. These limitations make it critical to discover new materials with high specific capacities augmented with the incessant need to engineer the materials exploiting economic scalable approaches to exhibit performance matching the theoretical predictions for rapid commercialization.

The focused search for finding new alternatives to the conventional Li – ion (Li metal oxide cathode-graphite anode) system has led to the identification of the Li-sulfur system with a theoretical specific capacity of 1672 mAh g^{-1} [2] as a promising candidate for high energy density lithium batteries. Sulfur being one of the most abundant elements on the Earth's crust has the additional advantages of being a promising low cost and environmentally benign material.

Despite these advantages, lithium-sulfur batteries suffer from several problems that prevent commercialization of the technology: (i) Sulfur has very low electronic conductivity ($\sim 10^{-17} \text{ S cm}^{-1}$) [3] which restricts complete utilization of the active material resulting in low specific capacity upon cycling, (ii) Unlike intercalation based Li – ion batteries, sulfur forms a non – intercalation reaction product Li_2S via a series of polysulfide (Li_2S_n ; $n = 2 - 8$) species leading to complex electrochemical reaction kinetics [4-12], (iii) These polysulfide intermediates show a range of solubility in organic electrolytes resulting in loss of active material [3, 10, 13-16], (iv) In

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4 addition, the dissolved polysulfides undergo crossover and coat the anode resulting in a gradual
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6 reduction in the cell voltage and subsequently leading to failure. These problems prevent the Li-
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8 S battery technology from being universally adopted and rapidly commercialized.
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11 Extensive research efforts with an objective of solving the problems plaguing Li – S batteries are
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13 primarily directed towards addressing the following key aspects: (i) Increasing the active
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15 material utilization by improving the electronic and ionic conductivity of sulfur electrodes
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17 through the use of conductive coatings or composites[17-35], (ii) Minimizing polysulfide
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19 dissolution by replacing the organic liquid electrolyte containing separator with a gel – polymer,
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21 composite – polymer or solid polymer electrolyte separator[20, 36-45] (iii) Complete
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23 replacement of the liquid based ionic conducting separator systems by solid lithium ion
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25 conducting electrolytes[46-48] (iv) Confinement of sulfur into the porous matrices preventing
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27 polysulfide entry into the liquid electrolyte phase[18, 23, 49-53].
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35 Efforts to improve the conductivity of sulfur are generally focused on either mixing with
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37 secondary conducting materials[19, 54, 55] or by utilizing the effect of crystallite size on
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39 macroscopic conductivity[21, 56-59]. However, these efforts mostly involve complex synthesis
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41 procedures or result in an increase in the inactive materials weight. On the other hand, use of
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43 solid and composite – polymer electrolytes [8, 20, 36-38, 60, 61] to replace the liquid electrolyte
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45 appears promising in ensuring polysulfide retention and preventing crossover, but is limited by
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47 the ionic conductivity of available solid state ionic conductors and the extreme handling issues
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49 associated with LISICON (Lithium Super Ionic Conductors) due to their air-sensitive nature and
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51 need for external activation[48, 62, 63]. Attempts aimed at preventing polysulfide from entering
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53 the liquid electrolyte phase generally focus on exploiting mesoporous and hollow carbonaceous
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55 materials as sulfur hosts [23, 49, 64-68].
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The strategy with such host-based strategies is two-pronged as described in the following: (a) the host acts as a conductive matrix; and (b) polysulfide species formed during lithiation are trapped within the host matrix. Use of MOF (Metal Organic Framework) derived carbon matrix following high temperature carbonization as a sulfur host [18, 69] has shown considerable improvement in cycling stability along with enhanced capacity. Recent reports on hosting sulfur into the carbon-based hosts have yielded improvement in stability[70-73]. Despite improvements in the improved stability, all these structures exhibit a high initial capacity loss and gradual capacity fade, the origin of which has not been studied.

To rationally design sulfur hosts using complex framework materials (CFM), a basic understanding of the mechanisms involved in trapping polysulfide into the host materials needs to be established. This mechanism would further explain the origin of irreversible capacity loss during the initial cycles. Thus, for the present studies, MOF – 5 was selected as the sulfur host due to its simple scalable synthesis procedure and very small pore size. In the present work, the 3-D sulfur impregnated nanoporous non-carbonized MOF prepared using a solution – infiltration technique is studied as cathodes in Li – S battery system. The electrochemical performance of the S – MOF was investigated using galvanostatic charge – discharge cycling. The work uses XPS analysis as a technique to understand the mechanism involved in masking polysulfide dissolution by directly binding the sulfide species onto the MOF. The proposed concept of using chemical bonding has been reported elsewhere although the complete prevention of polysulfide dissolution and retention by MOF structures has not been reported in the open literature to date, to the best of our knowledge[74].

MOF – 5 is a carbonate – based MOF with an average pore diameter of ~2.5 nm and is expected to bind with lithium polysulfides through a Lewis acid – base interaction[75]. The carbonization

process adopted in previous MOF based framework electrodes eliminates the possibility of such Lewis acid-base interactions, the presence of which is expected to cause binding of sulfur with the MOF structure ensuring polysulfide retention at the electrode surface. Moreover, these non-carbonized MOFs exhibit high pore volumes of $\sim 0.45 \text{ cm}^3 \text{ g}^{-1}$ [76] which can thus accommodate large quantities of sulfur. The use of an easy and facile room temperature synthesis method considerably adds to the scalability of the approach for generation of functional electrodes for entrapment of polysulfide. **Figure 1** provides a graphical representation of the synthesis and the sulfur encapsulation technique used in this work.

Zn – MOF – 5 was synthesized at room temperature. However, upon exposure to air, the Zn – MOF – 5 gets transformed into the corresponding air – stable phase, Zn – MOF – 5W. This MOF was then infiltrated with sulfur using a vapor infiltration technique. The sulfur infiltrated MOF, S – Zn – MOF using Zn^{2+} as the metallic center was used as cathodes for Li – S batteries. The S – Zn – MOF shows a very high initial capacity of 1476 mAh g^{-1} , which is one of the highest capacity values reported in the literature to date[55, 77, 78], stabilizing at 609 mAh g^{-1} over 200 cycles. The almost negligible fade rate ($0.0014\% \text{ cycle}^{-1}$) and complete prevention of polysulfide dissolution makes these cathode systems most promising candidates for Li-S batteries. However, there is an initial loss in capacity observed and to address this initial capacity loss observed in this system, studies related to the understanding of the mechanism involved in the electrochemical lithiation process is very much warranted.

The XPS technique was accordingly used to study polysulfide dissolution and to understand the S – C bonding providing insight into prevention of the polysulfide dissolution in the current work. The mechanistic overview provided in this report we believe could lay the foundations and further identify possible pathways for implementing future design strategies to enhance the

capacity and thus directly aim to resolve polysulfide dissolution problems plaguing the Li-S battery cathodes.

2. Experiments:

a) Preparation of MOF- 5 and Sulfur infiltration

Terephthalic acid ($C_6H_4 - 1, 4(COOH)_2$, 98%), Zinc acetate dihydrate ($Zn (CH_3CO_2)_2 \cdot H_2O$, >98%), Triethylamine ($(C_2H_5)_3N$, >99%), Dimethylformamide (DMF, 99.8%) and Chloroform ($CHCl_3$, 99.85%) were purchased from Sigma Aldrich and used as received. The Zn – MOF – 5W was synthesized using a modified room temperature precipitation method reported elsewhere [79, 80]. Accordingly, 20 mmoles of Terephthalic acid and 4 ml Triethylamine were dissolved in 200 ml DMF (**Solution 1**) and 50 mmoles zinc acetate dihydrate were dissolved in 200 ml DMF separately (**Solution 2**). The two solutions were then slowly mixed under stirring over 15 minutes to form a cloudy white solution. The colloidal solution obtained was continuously stirred for 12 h to form white precipitates of the MOF. The precipitates were then filtered and washed in DMF repeatedly. Solvent exchange was performed to ensure low-temperature pore-activation of the resultant MOF materials. DMF was also exchanged with chloroform by immersing in $CHCl_3$ for 7 days with replacement of fresh solvent every 24 h. The resulting white powder (MOF – 5 materials) were activated by heating at 110°C for 12 h.

Sulfur (~325mesh, Sigma Aldrich, Inc., 99% wt) was infiltrated into the MOF [81] under vacuum. Accordingly, pre – calculated weights of sulfur and MOF (50: 50 wt %) were sealed in a quartz tube under vacuum and heated at 300°C for 24 h allowing for impregnation of the sulfur into the MOF to generate the sulfur infiltrated S – Zn – MOF.

b) Materials Characterization and Electrochemical Measurements:

The synthesized MOF – 5W and S – MOF materials were characterized by X- ray diffraction using the Philips XPERT PRO system employing $\text{CuK}\alpha$ ($\lambda = 0.15406$ nm). The scans were typically recorded in 2θ range of 5° - 40° , setting the current and voltage constant at 40 mA and 45 kV respectively. The microstructure and morphology of the MOF – 5W and S – MOF materials was analyzed using High Resolution Transmission Microscopy (HRTEM) performed on a JEOL JEM2100F which features high resolution and rapid data acquisition.

The surface chemistry of the MOF and S – MOF was probed by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 Xi system (Thermo Scientific) equipped with a monochromated Al $\text{K}\alpha$ X-ray source. Uniform charge neutralization was provided by beams of low-energy (≤ 10 eV) Ar^+ ions and low-energy electrons guided by magnetic lens. The standard analysis spot of $400 \times 400 \mu\text{m}^2$ was defined by the microfocused X-ray source. The measurements were performed at room temperature in an ultra-high vacuum (UHV) chamber with the base pressure $< 5 \times 10^{-10}$ mbar (the charge neutralization device produced 2×10^{-10} mbar partial pressure of Ar during measurements). The binding energy (BE) scale of the analyzer was calibrated to produce < 50 meV deviations of the three standard peaks from their standard values: 83.98 eV for Au $4f_{7/2}$, 368.26 eV for Ag $3d_{5/2}$, and 932.67 eV for Cu $2p_{3/2}$. The aliphatic C1s peak was observed at 284.6 eV. High-resolution elemental XPS data in C2p, S2p and Zn2p regions were acquired with the analyzer pass energy set to 20 eV (corresponding to energy resolution of 0.36 eV) and the step size set to 0.1 eV. The Advantage software package (Thermo Fisher Scientific) was used to fit the elemental spectra based on calibrated analyzer transmission functions, Scofield sensitivity factors, and effective attenuation lengths for photoelectrons from the standard TPP-2M formalism.

The pore characteristics and specific surface area (SSA) of the samples were analyzed using a Micromeritics ASAP 2020 Physisorption analyzer, utilizing the Brunauer–Emmett–Teller (BET) isotherm generated. The powders were first vacuum degassed and then tested for nitrogen adsorption and desorption for surface area analysis.

Electrodes for battery half-cell characterization were prepared by casting a slurry of 70 wt% S – MOF, 20 wt% carbon black (super-P) and 10 wt% PVdF in N- Methyl Pyrrolidone (NMP) onto aluminum foil followed by drying under vacuum for 24 h. A uniform electrode loading of 1.5 mg – 2 mg cm² was maintained for all the electrochemical measurements. Control electrodes of commercially obtained sulfur powder (~325mesh, Sigma Aldrich, Inc, 99% wt) were prepared using identical composition and tested under identical conditions for comparison.

2025 – type coin cells were assembled in an Innovative, Inc. glove box (UHP Argon, <0.1 ppm O₂, H₂O) using S – MOF or commercial sulfur coated electrodes as working electrode, lithium foil as the counter electrode, Celgard polypropylene as the separator and 1.8 M LiCF₃SO₃ (lithium trifluoro-methanesulfonate) in 1:1 vol% 1, 3 dioxolane and 1, 2 dimethoxyethane with 0.1 M LiNO₃ as the electrolyte. The electrochemical cycling behavior of the cells thus prepared was studied by cycling between 1.7 – 2.6 V (wrt Li⁺/Li) at 0.2 C (~300 mA/g) current rate using an Arbin BT200 battery testing system. Finally, cyclic voltammetry (CV) measurements of the electrochemical cells were performed using (VersaSTAT 3, Princeton Applied Research) in the potential range of 1.7V – 2.6V at a scan rate of 0.1mV s⁻¹ to obtain mechanistic understanding.

3. Results and Discussion:

Crystallographic information file (CIF) obtained from MOFionics (CCDC number 256965) was used to simulate the XRD pattern of MOF – 5 which was used for comparison with the

experimentally observed patterns. **Figure 2** compares the experimental XRD patterns obtained for Zn – MOF – 5 (damp) with chloroform against the simulated pattern of Zn-MOF-5. The perfect fit between the simulated and experimental patterns indicates the single crystallinity and phase purity of the synthesized MOF – 5 materials, which is in-line with previous reports on MOF-5 materials[76, 80, 82-84]. The short-range order offered by the synthetic metal organic nanostructures can be observed from the presence of the crystalline diffraction peaks observed at low 2θ values[85-88].

However, upon exposure to ambient atmosphere i.e. complete desiccation and removal of the solvent, the MOF – 5 systems adsorb atmospheric moisture and undergoes slow transformation into hydrated phase MOF – 5W [89] through partial cleavage of the Zn-O bonds. This transformation is observed in Zn – MOF – 5 samples occurring because of handling in air during analysis and sample processing for infiltration. **Figure 2** shows the XRD profile of the MOF exposed to atmosphere compared with the damp or wet sample. The patterns of the MOF, MOF – 5W closely match those of published patterns for MOF – 5W [89] indicating the initial stages of hydration of MOF – 5. However, the Lewis – acid base interactions are observed in both MOF – 5 and MOF – 5W due to the presence of identical ligands irrespective of hydration[89] These MOF – 5W materials were further characterized and infiltrated with sulfur.

Table 1 represents the BET specific surface area and average pore sizes of the MOF – 5W materials. Zn – MOF – 5W exhibit a very high surface area of $\sim 684.25 \text{ m}^2 \text{ g}^{-1}$, with an average pore size of $\sim 2.47 \text{ nm}$. The MOF was found to have high pore volume of $\sim 0.422 \text{ cm}^3 \text{ g}^{-1}$. These values are in accordance with the values reported in the literature for MOF materials[90-92] shown in **Table 1**, though the values are somewhat lower than the Langmuir surface areas[80] reported for pure MOF-5 materials due to the transformation into MOF-5W

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4 It is however, noteworthy that these specific surface areas are greater than those of most
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6 carbonaceous host materials that have reportedly been used as sulfur hosts in Li – S batteries[18,
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8 49, 50, 65]. The large pore volume of the MOF materials is expected to facilitate in ensuring
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10 larger amounts of sulfur encapsulation and thus, resulting in high sulfur loading in the electrodes.
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12 Another unique advantage yielded using MOF materials to encapsulate sulfur is the small
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14 average pore diameter of the MOF (2.46 nm) that aids in minimizing polysulfide dissolution by
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16 offering a better mode for trapping and confining the polysulfide species.
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22 The thermal stability of MOF – 5W has been extensively studied and reported in the literature
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24 [93-95]. MOF – 5W exhibits exceptional stability up to 450°C (**Figure S1**), and hence, no
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26 denaturing is expected to occur during sulfur infiltration at 300°C which is confirmed by XRD
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28 analysis (**Figure 3**). XRD pattern of S – MOF show peaks corresponding to the MOF – 5
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30 materials (after exposure to air) (see **Figure 2**) along with sulfur peaks confirming the presence
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32 of sulfur in S – MOF and that the MOF is indeed not denatured during the sulfur infiltration
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34 process.
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40 It can be seen from above that the XRD analysis confirms the presence of sulfur along with the
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42 MOF. However, no detailed information regarding the chemical interaction of sulfur with the
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44 MOF host could be ascertained from the XRD patterns. The nature of sulfur in the S – MOF was
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46 thus, studied using XPS analysis (**Figure 4**). XPS analysis was performed on a Thermo
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48 ESCALAB 250Xi with suitable background correction. It can be observed that the characteristic
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50 S2p_{1/2} peak is observed for the commercial sulfur powder at 165.21 eV in line with previous
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52 reports for orthorhombic sulfur (S₈) [81, 96-98].
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57 The XPS spectra of S-MOF however, show a shift in the S2p peak as compared to commercial
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59 sulfur indicating the absence of free elemental sulfur suggesting binding of sulfur to the MOF
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structures. The S2p_{3/2} peak position at 162.45 eV corresponding to the binding of sulfur onto the MOF is similar to values observed in chemically-bound sulfur studied by Chehimi et al.,[99] further confirming the bound nature of sulfur onto the MOF. The nature of this interaction could be explained by the acidic nature of MOF – 5 precursors that tend to interact with the basic molecules of sulfur[75]. This interaction is more pronounced in gases even at room temperature [76, 100-103], because of which MOF – 5 is widely used for gas storage. This chemical binding of sulfur along with the nanoporous nature of the MOF would result in minimal sulfur dissolution into the organic liquid electrolyte. The shift in S2p_{3/2} peaks in S – MOF could alternatively be attributed to the distortion of sulfur within the MOF structures due to constraints imposed by the nanopores which could restrict the departure of sulfur from the pore during lithiation/delithiation[104]. This effect has also been observed in sulfur entrapped in single wall carbon nanotubes (SWCNTs) of ~1.5nm diameter by Fujimori et al [81] wherein sulfur adopts either a linear or a zig-zag orientation as opposed to the conventional cyclic S₈ rings of S. Due to an average pore size of 2 nm, comparable to the SWCNTs (~2 nm) used[81], the sulfur strands might experience strain from the MOF pore walls thus yielding a lower S2p binding energy.

MOF -5W, being derived from dicarboxylic acid molecules linking metal oxide cage, undergoes Lewis acid – base interaction with the polysulfides eventually binding them[75]. This kind of acid – base interactions have been reported in different systems involving molecular binding onto MOF[105, 106]. The complete trapping of the polysulfide in a host matrix however, has not yet been reported in the literature to the best of our knowledge and it is expected that further optimization of the MOF materials using a mechanistic understanding gained from the rest of this study would help engineer very high capacity cathodes with almost no capacity fade.

To prove the nanoporous nature of MOF and the binding of sulfur to MOF, TEM analysis was conducted (**Figure 5**). The TEM images of Zn-MOF – 5W at a lower magnification (**Figure 5a**) shows the highly porous nature of the MOF. Phase contrast image of S – Zn – MOF (**Figure 5b**) clearly shows ~5nm islands of sulfur inside the parent MOF structure thereby supporting the results from XRD analysis indicating sulfur infiltration into the MOF. **Figure 5c** demonstrates the local-ordering in the MOF structure resulting in the low-angle peaks observed in the X-ray diffraction pattern of Zn-MOF-5W in **Figure 2**. The nature of sulfur inside the MOF structure can be seen in **Figure 5d** wherein clear lattice fringes corresponding to crystalline sulfur infiltrated within the MOF structure are observed.

Having identified the clear presence of chemical bonding between the sulfur and the MOF matrix, the effect of this binding on the electrochemical performance of S – MOF was studied by performing electrochemical charge – discharge cycling. The electrochemical cycling performance of S – MOF is shown in **Figure 6**. The S – MOF and commercial sulfur electrodes were cycled at 0.2C with an average electrode loading of 1.5 – 2 g cm⁻² electrode area. The S – Zn – MOF shows an initial discharge capacity of 1476 mAh g⁻¹ which stabilizes at 624 mAh g⁻¹ after the 10th cycle. Upon prolonged cycling, the S – Zn – MOF shows a very stable capacity of 609 mAh g⁻¹ for over 200 cycles.

However, commercial sulfur showed an initial capacity of 800 mAh g⁻¹ which fades to less than 100 mAh g⁻¹ in less than 20 cycles. The nature of the cycling behavior is quite disparate between the two different electrodes with commercial sulfur failing almost instantaneously due to the well-known polysulfide formation and lack of entrapment of the same. The S-MOF electrodes on the other hand, undergo an initial fade followed by stabilization with the S-Zn-MOF demonstrating a superior fade-free cycling behavior (0.0014 % cycle⁻¹). The S-MOF electrode,

thus demonstrate exceptional stability[75] which could possibly be attributed to sulfur binding with the MOF (evidenced by XPS and TEM-**Figure 4** and **Figure 5d**) and resulting in effective trapping of polysulfide inside the nanopores of the MOF.

Though the MOF material exhibits excellent cycling stability after initial stabilization, a significant portion of the initial observed capacity is lost within the 1st ten cycles. This loss is typically attributed to the dissolution of sulfur into the electrolyte and loss of the eventual polysulfide species. However, the stabilization of the capacity following the initial loss appears to draw credence to the possibility of the confinement occurring but also alluding to the possible existence or evidence of other extraneous sacrificial or parasitic reactions. This result thus implied that the origin of the initial capacity loss in these S – MOF needs to be better understood warranting better characterization to be conducted to be able to improve the overall performance of the MOF based sulfur electrode system.

The effect of sulfur encapsulation within the MOF structures on the cycling performance of S – MOF was studied by analyzing the separators retrieved using XPS after 200 charge – discharge cycles. S2p peaks were analyzed to understand the nature of the sulfur/polysulfide species present in the various separators. As control experiments, the commercial separator and commercial separator dipped in the lithium electrolyte were also analyzed and the resultant XPS plots are shown in **Figure 7**. As expected, the Celgard separator does not display an S2p peak before cycling while a distinct peak corresponding to the electrolyte species (Trifluoro methyl sulfonate lithium salt) is seen in **Figure 7**[107]. The XPS plot for the post-cycled separator for the commercial sulfur electrode clearly shows S2p peaks at 169eV, 166.02 eV and 161.45 eV. The peak at 169eV corresponds to S2p peak of electrolyte CF_3SO_3^- . On the other hand, the peaks at 166.02 eV and 161.45 eV are due to lower and higher order polysulfide, respectively [10, 108-

110]. This indicates and validates the well-known phenomenon of the commercial sulfur electrode (**Figure 7**) undergoing rapid loss in capacity as seen in **Figure 6** due to the rapid dissolution of polysulfide species formed because of a lack of any medium or mechanism to retain/constrict the same at the electrode surface.

However, the separators corresponding to the S – MOF electrodes (post-cycling) (**Figures 7**) distinctly display only a single S2p peak at 169 eV which corresponds to the sulfur corresponding to the LiCF_3SO_3 from the electrolyte[107] as observed in the case of **Figure 7** for the commercial separator soaked in the electrolyte. The absence of any detectable polysulfide and elemental sulfur in the post-cycled separators cycled from the electrode generated with S-Zn-MOF, after cycle 1 (**Figure S4**), cycle 20 (**Figure S4**) and after 200 cycles (**Figures 7**) indicates complete constriction of the formed polysulfide within the MOF structures possibly due to chemical-binding of S to the MOF architecture as observed in the TEM images (**Figure 5**) and XPS (**Figure 4**). In addition, spatial confinement (**Table 1**) possibly aids in ensuring polysulfide retention at the electrode. Furthermore, absence of polysulfide species on the counter electrode (lithium) (**Figure S7**) after cycle 1, and 20 corroborates the constriction of electrochemically active sulfur species in the S-MOF electrode architecture. Porous structures have previously been shown to result in improved cycling behavior[18, 49, 65, 111]. However, complete masking of polysulfide dissolution using a porous host has seldom or never been reported to the best of our knowledge. The unique cage-like structure of the MOF along with the chemical binding occurring therein thus results in a very stable cycling performance with a remarkably low fade rate of $\sim 0.0014\% \text{ cycle}^{-1}$.

To understand the reasons for the observed electrochemical behavior and superior capacity retention, XPS analysis was performed on the S-Zn-MOF electrodes before cycling and after 200

charge-discharge cycles at a 0.2 C rate. **Figure 8** represents the C1s spectrum of slurry cast S – MOF electrodes and the same electrodes post cycling. S – Zn – MOF (**Figure 8**) electrode sample have peaks corresponding to – (CF₂ – CF₂) – bonds from PVdF binder (289.87 eV)[112], –C₆H₅S- bond corresponding to ring C – S interactions (285.59 eV)[113] and –C₆H₄S₂- (284.4 eV)[114]. The presence of the C-S peaks herein confirms the observations in the S2p spectrum (**Figure 4**) and corroborates the hypothesis that sulfur-carbon bonding aids in ensuring superior polysulfide retention within the MOF structure. The S – MOF post-200 cycles showed two C_{1s} peaks at 292.41 eV and 289.55 eV in addition to the peaks observed before cycling. The peak at 292.41 eV corresponds to the CF₃SO₃[–][107] group of the lithium salt LiCF₃SO₃ used with the organic electrolyte. The peak at 289.55 eV (**Figure 8**) corresponds to Li₂CO₃[115] resulting from the irreversible reaction of Li⁺ ions with the –(CO₃)– groups of the MOF [**Figure S8** depicts the C1s spectra of the MOF powders before and after sulfur infiltration indicating the presence of – (CO₃)– bonds therein which is to be expected given the structure of the MOF materials (**Figure 1**)]. The lithium carbonates may also be arising from the formation of a solid electrolyte interphase (SEI) layer at the electrode surface. The existence of carbonate moieties in the MOF materials both before and after cycling (occurs during cycles 1, 20 as well-see **Figure S5**) plays a role in the electrochemical characteristics of the MOF materials as will be discussed below.

Though the S-Zn-MOF material exhibit very stable cycling, they undergo an unusual initial loss in capacity. The XPS results discussed above clearly indicate that this loss is not related to polysulfide dissolution as evidenced by the lack thereof of any sulfur species detected on the separators (**Figure 7**). The presence of C-S bonding (**Figure 4, Figures 8**) in the MOF structure has been shown to result this unique behavior causing the very stable cycling after initial fade (**Figure 6**).

To understand the origin of this observed initial capacity loss, cyclic voltammetry was performed in the S-Zn-MOF (see **Figure 9**) electrodes at a very slow scan rate of 0.1 mV/s. A distinct change in peak position and height is observed in the cyclic voltammograms of S-Zn-MOF during cycling, especially between the 1st and 2nd cycles. In the case of the MOF material, a third anodic peak appears after the first cycle. This is actually the result of overlap of the two sulfur anodic processes (Reactions (i), (ii)) during the 1st cycle which has been known to result in the formation of one large peak at about 2.55 V[116]. A slight drop in overpotentials (**Table S1**) for the four reactions listed below (Reaction (i-iv)) is also observed, which is the result of a slight decrease in overpotentials for lithation and delithation, after the 1st cycle as reported elsewhere[116]. A third peak at ~2.28 V (**Table S1**) appears as a minor shoulder in S-Zn-MOF. The intensity of this shoulder peak stabilizes before the 10th cycle in the case of the S-Zn-MOF (**Figure 9**).

Though the third peak at ~2.28 V has not been explicitly reported in cyclic voltammograms in the literature, we believe the origin for this peak is the result of electrochemical oxidation of sulfur by the carbonate species present in the MOF structure. The chemical oxidation of sulfur to $\text{S}_2\text{O}_3^{2-}$ species and sulfate species has been reported in the literature[117]. Several studies[118] have also reported consumption of sulfur polysulfides to form –SCO– compounds in carbonate based electrolytes and this phenomenon, we believe, is reflected in the cyclic voltammograms as an electrochemical oxidation of the active sulfur as seen in **Figure 9**.

This hypothesis was further examined by XPS performed on the S – MOF coated electrodes before and after 200 cycles. **Figure 10** depicts the S2p profiles of the S-MOF electrodes before and after cycling. S – Zn – MOF electrode before cycling shows S2p peak at 162.45 eV representing the bonding of sulfur to MOF (as also observed in **Figure 4**). The S – Zn – MOF electrode post-cycling however, shows the presence of a satellite peak at 170.20 eV, corresponding to the occurrence of sulfur-carbon bonding [113, 119]. This indicates that sulfur is bound to the carbon before cycling as well as through the various stages of cycling preventing the loss of sulfur through the traditional polysulfide run-away to bulk electrolyte during cycling resulting in the exceptional stability observed in **Figure 6**. In addition to the peaks corresponding to C-S bonding, there are unique peaks observed in the post-cycled electrodes corresponding to the formation of -SCO- bonding[107] and a mixture of sulfate species (Li_2SO_4 at 168.45 eV[120] and ZnSO_4 [121, 122] represented by the peak at 168.90 eV). The irreversible loss in capacity observed in **Figure 6** could thus be attributed to irreversible consumption of sulfur through the formation of lithium, zinc sulfates during electrochemical cycling. The peak observed in the cyclic voltammograms at ~2.28 V in S-Zn-MOF material (**Figures 9** and **Table S1**) indicates that the formation of sulfates is an electrochemical process with no reversibility in the cycling window. The deactivation of the electrochemically active sulfur occurs through the formation of sulfate species and -SCO- compounds during the initial cycling resulting in irreversible capacity loss. This process occurs predominantly during the 1st ten cycles over which the cyclic voltammograms stabilizes as seen in **Figure 9**. The same is confirmed by examining the S2p peaks during the 1st, 20th and 200th cycle-see **Figure 10** and **Figure S6** where the occurrence of sulfate and sulfite species is seen in the 1st and 20th cycle as also seen to occur in the 200th cycle.

Thus, from the above it can be construed that the initial loss in capacity is attributed to phase transformation associated with chemical reaction between the polysulfide and the carbonate groups of the terephthalic sub – units of the MOF rather than the traditionally well-known polysulfide dissolution. Jie et al [123] used sulfur K – edge X-ray absorption spectroscopy to explain the chemical reaction of polysulfide with carbonate based ether electrolytes which was later confirmed by Zhe et al[124] in their work on cycling FeS_2 cathodes with ether based electrolytes. Taeun et al[118] observed decomposition of carbonate electrolytes by inter/intra molecule nucleophilic substitution to form -SCO- bonding[118].

The amount of sulfur that gets converted to sulfate corresponds [indicated by the initial irreversible loss in capacity (~59%)] well with the S: O ratio (2:1) based on the initial nominal composition used for the synthesis of the S-MOF (indicating that ~50% of the sulfur is rendered inactive through binding with oxygen existing within the MOF) (see **Supplementary information** for possible reaction mechanism **Reactions S1 and S2**).

A detailed study to overcome this oxidation phenomenon is currently ongoing and will be published shortly. Nevertheless, the results presented herein clearly demonstrate that the embedding of sulfur into the nanoporous MOF frameworks directly in the as-prepared form without any carbonization step ensures minimal polysulfide transport out of the electrode into the separator ensuring minimal capacity loss due to chemical bonding of carbon in the MOF structure with sulfur; and possible constriction of the lithium polysulfide species within the porous matrix. This is indeed reflected resulting in stable capacity of $\sim 609 \text{ mAh g}^{-1}$ with a fade rate of only $\sim 0.0014\% \text{ cycle}^{-1}$ demonstrating the promise of this novel synthetic strategy.

However, what is distinctly evident and observed from the results discussed in the present study is the presence of carbonate groups in the MOF that contribute to the formation of metal sulfate

type compounds during the initial charge – discharge cycle, resulting in the irreversible capacity loss during the initial cycling stages and not due to the hitherto accepted occurrence of dissolved polysulfide species. The results discussed herein also suggest that the use of carbonate – free MOF as potential hosts for sulfur in Li – S battery could result in electrodes with high capacity and exceptional stability. This discovery of sulfur interacting with MOF as outlined in the current study during synthesis and upon lithiation provides the framework outlining the pathway for a better understanding of the mechanism involved in the lithiation of sulfur encapsulated in the non-carbonized metal organic framework structures.

4. Conclusions:

Nanoporous non-carbonized MOF were synthesized using a simple, scalable room temperature method. Sulfur was directly infiltrated into the as-synthesized MOF with no subsequent carbonization and tested as cathodes for Li – S batteries. The resultant S – MOF display very high initial capacity (1476 mAh g^{-1}) that is rendered stable at 609 mAh g^{-1} for over 200 cycles with an impressive very minimal fade rate ($0.0014 \% \text{ cycle}^{-1}$). The study reveals that the use of non-carbonized MOF resulting in Lewis acid-base interactions is vital for ensuring the carbon-sulfur bonding with the MOF architecture resulting in complete retention of lithiated polysulfide species within the porous MOF structure. Furthermore, the results conclusively indicate that the use of a porous sulfur host is a critical factor for masking the generated polysulfide from escaping into the bulk electrolyte, resulting in the continuous loss in capacity ubiquitous to Li-S electrodes. There is however, an initial loss in capacity which is attributed to sulfur oxidation via reaction with carbonate groups in the MOF architecture to form sulfate species as confirmed by XPS and electrochemical studies. The absence of polysulfide species on the separators and counter electrodes following cycling clearly highlights the potential of nanoporous non-

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4 carbonized MOF materials as hosts for sulfur while establishing the importance of chemical
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6 bonding as well as pore-driven constriction in stabilizing the electrochemically active sulfur. The
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8 study also provides insights into preventing polysulfide dissolution using porous carbon-sulfur
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10 containing hosts. This understanding could pave the way for better engineering of metal organic
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12 frameworks as effective polysulfide traps ensuring the generation and stabilization of high
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14 capacity Li-S electrodes.
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18 19 20 **5. Acknowledgments**

21
22 Research supported by the U.S. Department of Energy OVT-DE-EE0006825. PNK thanks the
23
24 Edward R. Weidlein Chair Professorship Funds and the Center for Complex Engineered
25
26 Multifunctional Materials (CCEMM) as well as NSF-CBET 1511390 for partial assistance and
27
28 help with procuring the electrochemical equipment and facilities used in this research work. The
29
30 authors acknowledge Dr. Joel Gillespie, PPG Materials Characterization Laboratory, and the
31
32 Department of Chemistry for graciously providing access to the use of XPS instrumentation. The
33
34 authors also acknowledge the help of Mr. Karthikeyan Saravanan and Dr. John Keith,
35
36 Department of Chemical Engineering, University of Pittsburgh for their help with the simulation
37
38 of XRD profiles from CIF (Crystallographic Information File) information.
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44 45 **6. References:**

- 46
47
48 [1] M.D. Marca, Battery Cathodes, Batteries for Sustainability, Springer 2013.
49 [2] L.F. Nazar, M. Cuisinier, Q. Pang, Lithium-sulfur batteries, MRS Bulletin, 39 (2014) 436-442.
50 [3] Y. Yang, G. Zheng, Y. Cui, Nanostructured sulfur cathodes, Chemical Society Reviews, 42 (2013) 3018-
51 3032.
52 [4] S.S. Zhang, Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and
53 solutions, Journal of Power Sources, 231 (2013) 153-162.
54 [5] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, Li-O₂ and Li-S batteries with high energy
55 storage, Nature Materials, 11 (2012) 19-29.
56 [6] J. Cabana, L. Monconduit, D. Larcher, M. Rosa Palacin, Beyond Intercalation-Based Li-Ion Batteries:
57 The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions,
58 Advanced Materials, 22 (2010) E170-E192.
59
60
61
62
63
64
65

- [7] B. Scrosati, J. Garche, Lithium batteries: Status, prospects and future, *Journal of Power Sources*, 195 (2010) 2419-2430.
- [8] K. Jeddi, K. Sarikhani, N.T. Qazvini, P. Chen, Stabilizing lithium/sulfur batteries by a composite polymer electrolyte containing mesoporous silica particles, *Journal of Power Sources*, 245 (2014) 656-662.
- [9] V.S. Kolosnitsyn, E.V. Karaseva, Lithium-sulfur batteries: Problems and solutions, *Russian Journal of Electrochemistry*, 44 (2008) 506-509.
- [10] X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, L.F. Nazar, A highly efficient polysulfide mediator for lithium-sulfur batteries, *Nat Commun*, 6 (2015).
- [11] C.-N. Lin, W.-C. Chen, Y.-F. Song, C.-C. Wang, L.-D. Tsai, N.-L. Wu, Understanding dynamics of polysulfide dissolution and re-deposition in working lithium-sulfur battery by in-operando transmission X-ray microscopy, *Journal of Power Sources*, 263 (2014) 98-103.
- [12] M. Vijayakumar, N. Govind, E. Walter, S.D. Burton, A. Shukla, A. Devaraj, J. Xiao, J. Liu, C. Wang, A. Karim, S. Thevuthasan, Molecular structure and stability of dissolved lithium polysulfide species, *Physical Chemistry Chemical Physics*, 16 (2014) 10923-10932.
- [13] K.H. Wujcik, T.A. Pascal, C. Pemmaraju, D. Devaux, W.C. Stolte, N.P. Balsara, D. Prendergast, Characterization of Polysulfide Radicals Present in an Ether-Based Electrolyte of a Lithium-Sulfur Battery During Initial Discharge Using In Situ X-Ray Absorption Spectroscopy Experiments and First-Principles Calculations, *Advanced Energy Materials*, 5 (2015).
- [14] T.A. Pascal, K.H. Wujcik, J. Velasco-Velez, C. Wu, A.A. Teran, M. Kapilashrami, J. Cabana, J. Guo, M. Salmeron, N. Balsara, X-ray absorption spectra of dissolved polysulfides in lithium-sulfur batteries from first-principles, *The Journal of Physical Chemistry Letters*, 5 (2014) 1547-1551.
- [15] K.H. Wujcik, J. Velasco-Velez, C.H. Wu, T. Pascal, A.A. Teran, M.A. Marcus, J. Cabana, J. Guo, D. Prendergast, M. Salmeron, Fingerprinting Lithium-Sulfur Battery Reaction Products by X-ray Absorption Spectroscopy, *Journal of the Electrochemical Society*, 161 (2014) A1100-A1106.
- [16] J. Xiao, J.Z. Hu, H. Chen, M. Vijayakumar, J. Zheng, H. Pan, E.D. Walter, M. Hu, X. Deng, J. Feng, B.Y. Liaw, M. Gu, Z.D. Deng, D. Lu, S. Xu, C. Wang, J. Liu, Following the Transient Reactions in Lithium-Sulfur Batteries Using an In Situ Nuclear Magnetic Resonance Technique, *Nano Letters*, 15 (2015) 3309-3316.
- [17] W. Ahn, K.-B. Kim, K.-N. Jung, K.-H. Shin, C.-S. Jin, Synthesis and electrochemical properties of a sulfur-multi walled carbon nanotubes composite as a cathode material for lithium sulfur batteries, *Journal of Power Sources*, 202 (2012) 394-399.
- [18] R. Chen, T. Zhao, T. Tian, S. Cao, P.R. Coxon, K. Xi, D. Fairen-Jimenez, R. Vasant Kumar, A.K. Cheetham, Graphene-wrapped sulfur/metal organic framework-derived microporous carbon composite for lithium sulfur batteries, *APL Materials*, 2 (2014) 124109.
- [19] X. Duan, Y. Han, L. Huang, Y. Li, Y. Chen, Improved rate ability of low cost sulfur cathodes by using ultrathin graphite sheets with self-wrapped function as cheap conductive agent, *Journal of Materials Chemistry A*, 3 (2015) 8015-8021.
- [20] K. Jeddi, Y. Zhao, Y. Zhang, A. Konarov, P. Chen, Fabrication and Characterization of an Effective Polymer Nanocomposite Electrolyte Membrane for High Performance Lithium/Sulfur Batteries, *Journal of The Electrochemical Society*, 160 (2013) A1052-A1060.
- [21] C. Jia-jia, J. Xin, S. Qiu-jie, W. Chong, Z. Qian, Z. Ming-sen, D. Quan-feng, The preparation of nano-sulfur/MWCNTs and its electrochemical performance, *Electrochimica Acta*, 55 (2010) 8062-8066.
- [22] X. Ji, K.T. Lee, L.F. Nazar, A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries, *Nature Materials*, 8 (2009) 500-506.
- [23] J. Schuster, G. He, B. Mandlmeier, T. Yim, K.T. Lee, T. Bein, L.F. Nazar, Spherical Ordered Mesoporous Carbon Nanoparticles with High Porosity for Lithium-Sulfur Batteries, *Angewandte Chemie International Edition*, 51 (2012) 3591-3595.

- [24] X. Liang, Z. Wen, Y. Liu, H. Zhang, J. Jin, M. Wu, X. Wu, A composite of sulfur and polypyrrole–multi walled carbon combinatorial nanotube as cathode for Li/S battery, *Journal of Power Sources*, 206 (2012) 409-413.
- [25] J. Wang, L. Lu, D. Shi, R. Tandiono, Z. Wang, K. Konstantinov, H. Liu, A Conductive Polypyrrole-Coated, Sulfur–Carbon Nanotube Composite for Use in Lithium–Sulfur Batteries, *ChemPlusChem*, 78 (2013) 318-324.
- [26] C. Liang, N.J. Dudney, J.Y. Howe, Hierarchically Structured Sulfur/Carbon Nanocomposite Material for High-Energy Lithium Battery, *Chemistry of Materials*, 21 (2009) 4724-4730.
- [27] G. Zheng, Q. Zhang, J.J. Cha, Y. Yang, W. Li, Z.W. Seh, Y. Cui, Amphiphilic Surface Modification of Hollow Carbon Nanofibers for Improved Cycle Life of Lithium Sulfur Batteries, *Nano Letters*, 13 (2013) 1265-1270.
- [28] Y. Park, D.S. Shin, S.H. Woo, N.S. Choi, K.H. Shin, S.M. Oh, K.T. Lee, S.Y. Hong, Sodium terephthalate as an organic anode material for sodium ion batteries, *Advanced Materials*, 24 (2012) 3562-3567.
- [29] S. Evers, L.F. Nazar, New Approaches for High Energy Density Lithium–Sulfur Battery Cathodes, *Accounts of Chemical Research*, 46 (2012) 1135-1143.
- [30] C. Wang, K. Su, W. Wan, H. Guo, H. Zhou, J. Chen, X. Zhang, Y. Huang, High sulfur loading composite wrapped by 3D nitrogen-doped graphene as a cathode material for lithium–sulfur batteries, *Journal of Materials Chemistry A*, 2 (2014) 5018-5023.
- [31] W. Li, G. Zheng, Y. Yang, Z.W. Seh, N. Liu, Y. Cui, High-performance hollow sulfur nanostructured battery cathode through a scalable, room temperature, one-step, bottom-up approach, *Proceedings of the National Academy of Sciences*, 110 (2013) 7148-7153.
- [32] J.-Q. Huang, Q. Zhang, H.-J. Peng, X.-Y. Liu, W.-Z. Qian, F. Wei, Ionic shield for polysulfides towards highly-stable lithium-sulfur batteries, *Energy & Environmental Science*, 7 (2014) 347-353.
- [33] C. Xu, Y. Wu, X. Zhao, X. Wang, G. Du, J. Zhang, J. Tu, Sulfur/three-dimensional graphene composite for high performance lithium–sulfur batteries, *Journal of Power Sources*, 275 (2015) 22-25.
- [34] B. Li, S. Li, J. Liu, B. Wang, S. Yang, Vertically Aligned Sulfur–Graphene Nanowalls on Substrates for Ultrafast Lithium–Sulfur Batteries, *Nano Letters*, 15 (2015) 3073-3079.
- [35] S. Lu, Y. Chen, X. Wu, Z. Wang, Y. Li, Three-dimensional sulfur/graphene multifunctional hybrid sponges for lithium-sulfur batteries with large areal mass loading, *Scientific reports*, 4 (2014).
- [36] S.S. Jeong, Y.T. Lim, Y.J. Choi, G.B. Cho, K.W. Kim, H.J. Ahn, K.K. Cho, Electrochemical properties of lithium sulfur cells using PEO polymer electrolytes prepared under three different mixing conditions, *Journal of Power Sources*, 174 (2007) 745-750.
- [37] S.S. Zhang, D.T. Tran, A simple approach for superior performance of lithium/sulphur batteries modified with a gel polymer electrolyte, *Journal of Materials Chemistry A*, 2 (2014) 7383-7388.
- [38] Y. Zhao, Y. Zhang, D. Gosselink, T.N.L. Doan, M. Sadhu, H.-J. Cheang, P. Chen, Polymer Electrolytes for Lithium/Sulfur Batteries, *Membranes*, 2 (2012) 553-564.
- [39] G. Zhou, L. Li, D.W. Wang, X.y. Shan, S. Pei, F. Li, H.M. Cheng, A Flexible Sulfur-Graphene-Polypropylene Separator Integrated Electrode for Advanced Li–S Batteries, *Advanced Materials*, 27 (2015) 641-647.
- [40] H. Yao, K. Yan, W. Li, G. Zheng, D. Kong, Z.W. Seh, V.K. Narasimhan, Z. Liang, Y. Cui, Improved lithium–sulfur batteries with a conductive coating on the separator to prevent the accumulation of inactive S-related species at the cathode–separator interface, *Energy & Environmental Science*, 7 (2014) 3381-3390.
- [41] C.-H. Chang, S.-H. Chung, A. Manthiram, Ultra-lightweight PANiNF/MWCNT-functionalized separators with synergistic suppression of polysulfide migration for Li–S batteries with pure sulfur cathodes, *Journal of Materials Chemistry A*, 3 (2015) 18829-18834.
- [42] I. Bauer, S. Thieme, J. Brückner, H. Althues, S. Kaskel, Reduced polysulfide shuttle in lithium–sulfur batteries using Nafion-based separators, *Journal of Power Sources*, 251 (2014) 417-422.

- [43] S.H. Chung, A. Manthiram, Bifunctional Separator with a Light-Weight Carbon-Coating for Dynamically and Statically Stable Lithium-Sulfur Batteries, *Advanced Functional Materials*, 24 (2014) 5299-5306.
- [44] Y. Zhang, Y. Zhao, Z. Bakenov, D. Gosselink, P. Chen, Poly (vinylidene fluoride-co-hexafluoropropylene)/poly (methylethacrylate)/nanoclay composite gel polymer electrolyte for lithium/sulfur batteries, *Journal of Solid State Electrochemistry*, 18 (2014) 1111-1116.
- [45] M. Agostini, J. Hassoun, A lithium-ion sulfur battery using a polymer, polysulfide-added membrane, *Scientific reports*, 5 (2015).
- [46] A. Hayashi, T. Ohtomo, F. Mizuno, K. Tadanaga, M. Tatsumisago, All-solid-state Li/S batteries with highly conductive glass-ceramic electrolytes, *Electrochemistry Communications*, 5 (2003) 701-705.
- [47] Z. Lin, C. Liang, Lithium-sulfur batteries: from liquid to solid cells, *Journal of Materials Chemistry A*, 3 (2015) 936-958.
- [48] X. Yu, Z. Bi, F. Zhao, A. Manthiram, Hybrid Lithium-Sulfur Batteries with a Solid Electrolyte Membrane and Lithium Polysulfide Catholyte, *ACS Applied Materials & Interfaces*, 7 (2015) 16625-16631.
- [49] S.-R. Chen, Y.-P. Zhai, G.-L. Xu, Y.-X. Jiang, D.-Y. Zhao, J.-T. Li, L. Huang, S.-G. Sun, Ordered mesoporous carbon/sulfur nanocomposite of high performances as cathode for lithium-sulfur battery, *Electrochimica Acta*, 56 (2011) 9549-9555.
- [50] X. Li, Y. Cao, W. Qi, L.V. Saraf, J. Xiao, Z. Nie, J. Mietek, J.-G. Zhang, B. Schwenzer, J. Liu, Optimization of mesoporous carbon structures for lithium-sulfur battery applications, *Journal of Materials Chemistry*, 21 (2011) 16603-16610.
- [51] X. Liang, Z. Wen, Y. Liu, H. Zhang, L. Huang, J. Jin, Highly dispersed sulfur in ordered mesoporous carbon sphere as a composite cathode for rechargeable polymer Li/S battery, *Journal of Power Sources*, 196 (2011) 3655-3658.
- [52] Y.-S. Su, A. Manthiram, Lithium-sulphur batteries with a microporous carbon paper as a bifunctional interlayer, *Nat Commun*, 3 (2012) 1166.
- [53] J. Wang, S.Y. Chew, Z.W. Zhao, S. Ashraf, D. Wexler, J. Chen, S.H. Ng, S.L. Chou, H.K. Liu, Sulfur-mesoporous carbon composites in conjunction with a novel ionic liquid electrolyte for lithium rechargeable batteries, *Carbon*, 46 (2008) 229-235.
- [54] D.-W. Wang, Q. Zeng, G. Zhou, L. Yin, F. Li, H.-M. Cheng, I.R. Gentle, G.Q.M. Lu, Carbon-sulfur composites for Li-S batteries: status and prospects, *Journal of Materials Chemistry A*, 1 (2013) 9382-9394.
- [55] H. Wang, Y. Yang, Y. Liang, J.T. Robinson, Y. Li, A. Jackson, Y. Cui, H. Dai, Graphene-Wrapped Sulfur Particles as a Rechargeable Lithium-Sulfur Battery Cathode Material with High Capacity and Cycling Stability, *Nano Letters*, 11 (2011) 2644-2647.
- [56] S. Xin, L. Gu, N.-H. Zhao, Y.-X. Yin, L.-J. Zhou, Y.-G. Guo, L.-J. Wan, Smaller Sulfur Molecules Promise Better Lithium-Sulfur Batteries, *Journal of the American Chemical Society*, 134 (2012) 18510-18513.
- [57] L. Qiu, S. Zhang, L. Zhang, M. Sun, W. Wang, Preparation and enhanced electrochemical properties of nano-sulfur/poly(pyrrole-co-aniline) cathode material for lithium/sulfur batteries, *Electrochimica Acta*, 55 (2010) 4632-4636.
- [58] Y. Zhang, Y. Zhao, A. Konarov, D. Gosselink, H.G. Soboleski, P. Chen, A novel nano-sulfur/polypyrrole/graphene nanocomposite cathode with a dual-layered structure for lithium rechargeable batteries, *Journal of Power Sources*, 241 (2013) 517-521.
- [59] W. Zheng, Y.W. Liu, X.G. Hu, C.F. Zhang, Novel nanosized adsorbing sulfur composite cathode materials for the advanced secondary lithium batteries, *Electrochimica Acta*, 51 (2006) 1330-1335.
- [60] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature*, 414 (2001) 359-367.

- [61] M. Rao, X. Geng, X. Li, S. Hu, W. Li, Lithium-sulfur cell with combining carbon nanofibers–sulfur cathode and gel polymer electrolyte, *Journal of Power Sources*, 212 (2012) 179-185.
- [62] Y. Mo, S.P. Ong, G. Ceder, First Principles Study of the Li₁₀GeP₂S₁₂ Lithium Super Ionic Conductor Material, *Chemistry of Materials*, 24 (2012) 15-17.
- [63] M.J. Rice, W.L. Roth, Ionic transport in super ionic conductors: a theoretical model, *Journal of Solid State Chemistry*, 4 (1972) 294-310.
- [64] J. Guo, Y. Xu, C. Wang, Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium–Sulfur Batteries, *Nano Letters*, 11 (2011) 4288-4294.
- [65] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, Porous Hollow Carbon@Sulfur Composites for High-Power Lithium–Sulfur Batteries, *Angewandte Chemie*, 123 (2011) 6026-6030.
- [66] X. Ji, K.T. Lee, L.F. Nazar, A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries, *Nat Mater*, 8 (2009) 500-506.
- [67] C. Zhang, H.B. Wu, C. Yuan, Z. Guo, X.W. Lou, Confining Sulfur in Double-Shelled Hollow Carbon Spheres for Lithium–Sulfur Batteries, *Angewandte Chemie*, 124 (2012) 9730-9733.
- [68] G. Zheng, Y. Yang, J.J. Cha, S.S. Hong, Y. Cui, Hollow Carbon Nanofiber-Encapsulated Sulfur Cathodes for High Specific Capacity Rechargeable Lithium Batteries, *Nano Letters*, 11 (2011) 4462-4467.
- [69] H.B. Wu, S. Wei, L. Zhang, R. Xu, H.H. Hng, X.W. Lou, Embedding Sulfur in MOF-Derived Microporous Carbon Polyhedrons for Lithium–Sulfur Batteries, *Chemistry – A European Journal*, 19 (2013) 10804-10808.
- [70] J.H. Park, K.M. Choi, D.K. Lee, B.C. Moon, S.R. Shin, M.-K. Song, J.K. Kang, Encapsulation of redox polysulphides via chemical interaction with nitrogen atoms in the organic linkers of metal-organic framework nanocrystals, *Scientific Reports*, 6 (2016) 25555.
- [71] Z. Wang, B. Wang, Y. Yang, Y. Cui, Z. Wang, B. Chen, G. Qian, Mixed-Metal–Organic Framework with Effective Lewis Acidic Sites for Sulfur Confinement in High-Performance Lithium–Sulfur Batteries, *ACS Applied Materials & Interfaces*, 7 (2015) 20999-21004.
- [72] Z. Wang, X. Li, Y. Cui, Y. Yang, H. Pan, Z. Wang, C. Wu, B. Chen, G. Qian, A Metal–Organic Framework with Open Metal Sites for Enhanced Confinement of Sulfur and Lithium–Sulfur Battery of Long Cycling Life, *Crystal Growth & Design*, 13 (2013) 5116-5120.
- [73] J. Zhou, R. Li, X. Fan, Y. Chen, R. Han, W. Li, J. Zheng, B. Wang, X. Li, Rational design of a metal-organic framework host for sulfur storage in fast, long-cycle Li-S batteries, *Energy & Environmental Science*, 7 (2014) 2715-2724.
- [74] Z. Wang, Y. Dong, H. Li, Z. Zhao, H. Bin Wu, C. Hao, S. Liu, J. Qiu, X.W. Lou, Enhancing lithium–sulphur battery performance by strongly binding the discharge products on amino-functionalized reduced graphene oxide, *Nat Commun*, 5 (2014).
- [75] J. Zheng, J. Tian, D. Wu, M. Gu, W. Xu, C. Wang, F. Gao, M.H. Engelhard, J.-G. Zhang, J. Liu, J. Xiao, Lewis Acid–Base Interactions between Polysulfides and Metal Organic Framework in Lithium Sulfur Batteries, *Nano Letters*, 14 (2014) 2345-2352.
- [76] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, *Nature*, 402 (1999) 276-279.
- [77] X. Ji, L.F. Nazar, Advances in Li-S batteries, *Journal of Materials Chemistry*, 20 (2010) 9821-9826.
- [78] L.-X. Miao, W.-K. Wang, A.-B. Wang, K.-G. Yuan, Y.-S. Yang, A high sulfur content composite with core-shell structure as cathode material for Li-S batteries, *Journal of Materials Chemistry A*, 1 (2013) 11659-11664.
- [79] J. Li, S. Cheng, Q. Zhao, P. Long, J. Dong, Synthesis and hydrogen-storage behavior of metal–organic framework MOF-5, *International Journal of Hydrogen Energy*, 34 (2009) 1377-1382.
- [80] D.J. Tranchemontagne, J.R. Hunt, O.M. Yaghi, Room temperature synthesis of metal-organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0, *Tetrahedron*, 64 (2008) 8553-8557.

- [81] T. Fujimori, A. Morelos-Gómez, Z. Zhu, H. Muramatsu, R. Futamura, K. Urita, M. Terrones, T. Hayashi, M. Endo, S. Young Hong, Y. Chul Choi, D. Tománek, K. Kaneko, Conducting linear chains of sulphur inside carbon nanotubes, *Nat Commun*, 4 (2013).
- [82] Y. Liu, Z. Ng, E.A. Khan, H.-K. Jeong, C.-b. Ching, Z. Lai, Synthesis of continuous MOF-5 membranes on porous α -alumina substrates, *Microporous and Mesoporous Materials*, 118 (2009) 296-301.
- [83] W.-J. Son, J. Kim, J. Kim, W.-S. Ahn, Sonochemical synthesis of MOF-5, *Chemical Communications*, (2008) 6336-6338.
- [84] C. Zheng, H.F. Greer, C.-Y. Chiang, W. Zhou, Microstructural study of the formation mechanism of metal-organic framework MOF-5, *CrystEngComm*, 16 (2014) 1064-1070.
- [85] C. Chmelik, D. Freude, H. Bux, J. Haase, Ethene/ethane mixture diffusion in the MOF sieve ZIF-8 studied by MAS PFG NMR diffusometry, *Microporous and Mesoporous Materials*, 147 (2012) 135-141.
- [86] R. Zacharia, D. Cossement, L. Lafi, R. Chahine, Volumetric hydrogen sorption capacity of monoliths prepared by mechanical densification of MOF-177, *Journal of Materials Chemistry*, 20 (2010) 2145-2151.
- [87] K.V. Klementev, Extraction of the fine structure from x-ray absorption spectra, *Journal of Physics D: Applied Physics*, 34 (2001) 209.
- [88] V. Guillermin, S. Gross, C. Serre, T. Devic, M. Bauer, G. Férey, A zirconium methacrylate oxocluster as precursor for the low-temperature synthesis of porous zirconium(iv) dicarboxylates, *Chemical Communications*, 46 (2010) 767-769.
- [89] N.A. Rodriguez, R. Parra, M.A. Grela, Structural characterization, optical properties and photocatalytic activity of MOF-5 and its hydrolysis products: implications on their excitation mechanism, *RSC Advances*, 5 (2015) 73112-73118.
- [90] E.L. First, C.A. Floudas, MOFomics: Computational pore characterization of metal-organic frameworks, *Microporous and Mesoporous Materials*, 165 (2013) 32-39.
- [91] U. Ravon, M.E. Domine, C. Gaudillere, A. Desmartin-Chomel, D. Farrusseng, MOFs as acid catalysts with shape selectivity properties, *New Journal of Chemistry*, 32 (2008) 937-940.
- [92] J. Ren, D.E.C. Rogers, T. Segakweng, H.W. Langmi, B.C. North, M. Mathe, D. Bessarabov, Thermal treatment induced transition from $\text{Zn}_3(\text{OH})_2(\text{BDC})_2$ (MOF-69c) to $\text{Zn}_4\text{O}(\text{BDC})_3$ (MOF-5), *International Journal of Materials Research*, 105 (2013) 89-93.
- [93] S. Gadipelli, Z. Guo, Postsynthesis Annealing of MOF-5 Remarkably Enhances the Framework Structural Stability and CO_2 Uptake, *Chemistry of Materials*, 26 (2014) 6333-6338.
- [94] B. Liu, A.G. Wong-Foy, A.J. Matzger, Rapid and enhanced activation of microporous coordination polymers by flowing supercritical CO_2 , *Chemical Communications*, 49 (2013) 1419-1421.
- [95] C.-M. Wu, M. Rath, S.P. Ahrenkiel, R.T. Koodali, Z. Wang, Facile synthesis of MOF-5 confined in SBA-15 hybrid material with enhanced hydrostability, *Chemical Communications*, 49 (2013) 1223-1225.
- [96] X.-R. Yu, F. Liu, Z.-Y. Wang, Y. Chen, Auger parameters for sulfur-containing compounds using a mixed aluminum-silver excitation source, *Journal of Electron Spectroscopy and Related Phenomena*, 50 (1990) 159-166.
- [97] G. Hollinger, P. Kumurdjian, J.M. Mackowski, P. Pertosa, L. Porte, T.M. Duc, ESCA study of molecular GeS_3 -x TeAs_2 glasses, *Journal of Electron Spectroscopy and Related Phenomena*, 5 (1974) 237-245.
- [98] J.M. Thomas, I. Adams, R.H. Williams, M. Barber, Valence band structures and core-electron energy levels in the monochalcogenides of gallium. Photoelectron spectroscopic study, *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 68 (1972) 755-764.
- [99] M.M. Chehimi, M. Delamar, X-ray photoelectron spectroscopy of merocyanine dyes, *Journal of Electron Spectroscopy and Related Phenomena*, 50 (1990) C25-C32.
- [100] R.E. Morris, P.S. Wheatley, Gas Storage in Nanoporous Materials, *Angewandte Chemie International Edition*, 47 (2008) 4966-4981.
- [101] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, Hydrogen Storage in Microporous Metal-Organic Frameworks, *Science*, 300 (2003) 1127-1129.

- [102] E.V. Perez, K.J. Balkus Jr, J.P. Ferraris, I.H. Musselman, Mixed-matrix membranes containing MOF-5 for gas separations, *Journal of Membrane Science*, 328 (2009) 165-173.
- [103] S. Ma, H.-C. Zhou, Gas storage in porous metal-organic frameworks for clean energy applications, *Chemical Communications*, 46 (2010) 44-53.
- [104] C.-P. Yang, Y.-X. Yin, Y.-G. Guo, L.-J. Wan, Electrochemical (De)Lithiation of 1D Sulfur Chains in Li-S Batteries: A Model System Study, *Journal of the American Chemical Society*, 137 (2015) 2215-2218.
- [105] A.S. Munch, F.O.R.L. Mertens, The Lewis acidic and basic character of the internal HKUST-1 surface determined by inverse gas chromatography, *CrystEngComm*, 17 (2015) 438-447.
- [106] Z. Akimbekov, D. Wu, C.K. Brozek, M. Dinca, A. Navrotsky, Thermodynamics of solvent interaction with the metal-organic framework MOF-5, *Physical Chemistry Chemical Physics*, 18 (2016) 1158-1162.
- [107] B.J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, K. Siegbahn, Molecular Spectroscopy by Means of ESCA II. Sulfur compounds. Correlation of electron binding energy with structure, *Physica Scripta*, 1 (1970) 286.
- [108] C. Zu, Y. Fu, A. Manthiram, Highly reversible Li/dissolved polysulfide batteries with binder-free carbon nanofiber electrodes, *Journal of Materials Chemistry A*, 1 (2013) 10362-10367.
- [109] Y.-S. Su, Y. Fu, T. Cochell, A. Manthiram, A strategic approach to recharging lithium-sulphur batteries for long cycle life, *Nat Commun*, 4 (2013).
- [110] C. Zu, N. Azimi, Z. Zhang, A. Manthiram, Insight into lithium-metal anodes in lithium-sulfur batteries with a fluorinated ether electrolyte, *Journal of Materials Chemistry A*, 3 (2015) 14864-14870.
- [111] Z. Gong, Q. Wu, F. Wang, X. Li, X. Fan, H. Yang, Z. Luo, A hierarchical micro/mesoporous carbon fiber/sulfur composite for high-performance lithium-sulfur batteries, *RSC Advances*, 6 (2016) 37443-37451.
- [112] S. Dapoz, N. Betz, M.-J. Guittet, A. Le Moël, ESCA characterization of heparin-like fluoropolymers obtained by functionalization after grafting induced by swift heavy ion irradiation, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 105 (1995) 120-125.
- [113] J. Riga, P. Snauwaert, A. De Pryck, R. Lazzaroni, J.P. Boutique, J.J. Verbist, J.L. Brédas, J.M. André, C. Taliani, Electronic structure of sulphur-containing conducting polymers, *Synthetic Metals*, 21 (1987) 223-228.
- [114] D.R. Huntley, The mechanism of the desulfurization of benzenethiol by nickel (110), *The Journal of Physical Chemistry*, 96 (1992) 4550-4558.
- [115] A.S. Cavanagh, Y. Lee, B. Yoon, S. George, Atomic Layer Deposition of LiOH and Li₂CO₃ Using Lithium t-Butoxide as the Lithium Source, *ECS Transactions*, 33 (2010) 223-229.
- [116] M. Rao, W. Li, E.J. Cairns, Porous carbon-sulfur composite cathode for lithium/sulfur cells, *Electrochemistry Communications*, 17 (2012) 1-5.
- [117] N. Gobeltz, A. Demortier, J.P. Lelieur, C. Duhayon, Identification of the Products of the Reaction between Sulfur and Sodium Carbonate, *Inorganic Chemistry*, 37 (1998) 136-138.
- [118] T. Yim, M.-S. Park, J.-S. Yu, K.J. Kim, K.Y. Im, J.-H. Kim, G. Jeong, Y.N. Jo, S.-G. Woo, K.S. Kang, I. Lee, Y.-J. Kim, Effect of chemical reactivity of polysulfide toward carbonate-based electrolyte on the electrochemical performance of Li-S batteries, *Electrochimica Acta*, 107 (2013) 454-460.
- [119] J.A. Gardella, S.A. Ferguson, R.L. Chin, $\pi^* \leftarrow \pi$ Shakeup Satellites for the Analysis of Structure and Bonding in Aromatic Polymers by X-Ray Photoelectron Spectroscopy, *Appl. Spectrosc.*, 40 (1986) 224-232.
- [120] K.M. Abraham, S.M. Chaudhri, The Lithium Surface Film in the Li / SO₂ Cell, *Journal of The Electrochemical Society*, 133 (1986) 1307-1311.
- [121] B.R. Strohmeier, D.M. Hercules, Surface spectroscopic characterization of the interaction between zinc ions and γ -alumina, *Journal of Catalysis*, 86 (1984) 266-279.

- [122] V.I. Nefedov, A comparison of results of an ESCA study of nonconducting solids using spectrometers of different constructions, *Journal of Electron Spectroscopy and Related Phenomena*, 25 (1982) 29-47.
- [123] J. Gao, M.A. Lowe, Y. Kiya, H.D. Abruña, Effects of Liquid Electrolytes on the Charge–Discharge Performance of Rechargeable Lithium/Sulfur Batteries: Electrochemical and in-Situ X-ray Absorption Spectroscopic Studies, *The Journal of Physical Chemistry C*, 115 (2011) 25132-25137.
- [124] Z. Hu, K. Zhang, Z. Zhu, Z. Tao, J. Chen, FeS₂ microspheres with an ether-based electrolyte for high-performance rechargeable lithium batteries, *Journal of Materials Chemistry A*, 3 (2015) 12898-12904.
- [125] Y. Ming, J. Purewal, J. Yang, C. Xu, R. Soltis, J. Warner, M. Veenstra, M. Gaab, U. Müller, D.J. Siegel, Kinetic Stability of MOF-5 in Humid Environments: Impact of Powder Densification, Humidity Level, and Exposure Time, *Langmuir*, 31 (2015) 4988-4995.

Figures:

Figure 1: Schematic representation of the synthesis of MOF followed by sulfur infiltration.

Figure 2: XRD patterns of Zn – MOF – 5 predicted by simulation, experimentally synthesized Zn MOF – 5 post-exposure to atmospheric air.

Figure 3: XRD patterns of commercial Sulfur, MOF – 5W predicted by simulation, experimentally synthesized S – Zn – MOF.

Figure 4: XPS S₂p Binding Energy profile of Commercial Sulfur and S – Zn – MOF.

Figure 5a: TEM images of Zn – MOF– 5Wat higher magnification

Figure 5b: TEM images of S - Zn – MOF and lower magnification.

Figure 5c: TEM images of S-Zn-MOF – 5W at lower magnification.

Figure 5d: TEM image of S-Zn-MOF at higher magnification.

Figure 6: Cycling performance of S – Zn-MOF and commercial sulfur at 0.2C rate.

Figure 7: XPS S2p binding energy profile of commercial separator, commercial separator soaked in electrolyte; separators of commercial sulfur electrode and S–Zn–MOF (after 200 cycles at 0.2 C rate).

Figure 8: XPS C1s Binding Energy profile of slurry coated electrodes of S – Zn – MOF before cycling and S – Zn – MOF after 200 cycles at 0.2 C rate.

Figure 9: Cyclic Voltammetry Plot of S – Zn – MOF at 1st, 2nd, 10th and 20th cycles at a scan rate of 0.1mV s⁻¹.

Figure 10: XPS S2p Binding Energy profile of slurry coated electrodes of S – Zn – MOF- before cycling and S – Zn – MOF after 200 cycles at 0.2 C rate.

Tables:

	BET Surface Area/ m² g⁻¹	Langmuir Surface Area/ m² g⁻¹	Total Pore Volume/ cm³ g⁻¹	Adsorption average pore width/ nm	BET Surface Area/ m² g⁻¹ (literature)
Zn – MOF – 5W	684.25	1083.07	0.422	2.47	1100 – 2500 [90-92, 125]

Table 1: BET surface area and pore size analysis of Zn – MOF – 5W exposed to atmospheric moisture.