

Realizing High-Performance Li-S Batteries through Additive Manufactured and Chemically Enhanced Cathodes

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Numerous efforts are made to improve the reversible capacity and long-term cycling stability of Li-S cathodes. However, they are susceptible to irreversible capacity loss during cycling owing to shuttling effects and poor Li⁺ transport under high sulfur loading. Herein, a physically and chemically enhanced lithium sulfur cathode is proposed to address these challenges. Additive manufacturing is used to construct numerous microchannels within high sulfur loading cathodes, which enables desirable deposition mechanisms of lithium polysulfides and improves Li⁺ and e⁻ transport. Concurrently, cobalt sulfide is incorporated into the cathode composition and demonstrates strong adsorption behavior toward lithium polysulfides during cycling. As a result, excellent electrochemical performance is obtained by the design of a physically and chemically enhanced lithium sulfur cathode. The reported electrode, with a sulfur loading of 8 mg cm⁻², delivers an initial capacity of 1118.8 mA h g⁻¹ and a reversible capacity of 771.7 mA h g⁻¹ after 150 cycles at a current density of 3 mA cm⁻². This work demonstrates that a chemically enhanced sulfur cathode, manufactured through additive manufacturing, is a viable pathway to achieve high-performance Li-S batteries.

1. Introduction

The rapid development of the consumer electronics and electric vehicle sector has caused a booming demand for high-performance energy storage devices.^[1] However, practical application dictates that these energy storage systems must be intrinsically safe, possess high gravimetric and volumetric energy density, and have low-cost components. Hence, to date, lithium-ion batteries (LIBs) have dominated the frontline of energy storage solutions.^[2] Yet, LIBs are limited by their theoretical capacity, which are directly affected

by the constituent material properties.^[3] To address this issue, significant efforts have been made to improve the LIB anode. However, research and development of cathode materials in LIBs has yet to reach the level required for a significant boost in energy density.^[4–6] Hence, sulfur has been widely regarded as a promising cathode material owing to the high specific capacity (1672 mA h g⁻¹) enabled by the two-electron transfer process per sulfur atom. Lithium sulfur batteries (Li-S) can theoretically achieve energy densities nearly ten times that of commercial LIBs (2600 Wh K g⁻¹).^[7–10] Furthermore, the low-cost and nontoxic nature of sulfur greatly increases the practicality of Li-S batteries. However, there are three notable challenges which have prevented commercialization: 1) fast capacity fading owing to the dissolution of soluble lithium polysulfides (LiPS),

which shuttle across the electrodes and form undesirable by-products; 2) sulfur's poor electrical conductivity; and 3) a rigorous commercialization requirement for high sulfur loading of 3 mg cm⁻² or greater, while maintaining a high specific capacity and stable cycling performance.^[11–16]

Efforts to combat the major Li-S battery challenges highlighted above have led to the development of two general approaches at the electrodes: chemical and physical-based solutions.^[8,17] The chemical route has focused on the role of metal-based additives. Examples are metal oxides and sulfides, which have been reported to act as both a catalyst for the LiPS conversion reaction (Li₂S₈ to Li₂S) as well as a mechanism for chemical adsorption of LiPSs.^[6,18] For that reason, metal sulfides have been used to enhance electrochemical performance in various energy storage devices to date including Li-S batteries. For example, cobalt sulfide's success in catalyzing redox reactions in other energy storage solutions and its application as a catalyst in the Li-S battery was recently explored.^[18–21] For the physical methods, efforts have been focused on trapping LiPSs at the cathode through careful geometric design. Recently, multiple groups including our own have made efforts to use additive manufacturing (3D printing) to achieve tailored micro-scale geometry to promote faster ion or electron transfer.^[22–24] Other efforts in the field have also demonstrated the strong

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performance of electrodes enabled by the process' fine dimensional control.^[25–27]

The principal challenge that has yet to be fully addressed is the ability to maximize and maintain high specific energy and energy density when cycling.^[8,28] Although other factors such as long cycle life are of importance, the defining feature of the Li-S system is its theoretical potential for high energy density and specific energy. The most effective way of improving both criteria is by increasing the sulfur loading of the cell.^[29] However, the problem of sulfur's insulating properties and the polysulfide shuttling effect will be exacerbated by high sulfur loading. Hence, new techniques are required to optimize for both cycling stability and high sulfur loading.

Herein, to address the aforementioned challenges, this work used a dual-mechanism approach to develop a chemically and physically enhanced Li-S cathode. This study demonstrates the ability of additive manufacturing (AM) to design microarchitecture and its high control over the fabrication process. AM fabrication not only easily controls sulfur loading but also achieves fast ion and electron transfer within high sulfur loading cathodes. Concurrently, chemical enhancement was achieved by pairing a sulfur-carbon host with embedded CoS_x . This promoted simultaneous adsorption of LiPSs and its redox reaction. The resulting cathode is herein abbreviated 3DP-C/S/ CoS_x , where 3DP stands for 3D-printed. To our knowledge, this is the first effort to incorporate nanocatalysts directly as a facile additive to a carbon-sulfur cathodic ink in the Li-S system. A similar cathode to

3DP-C/S/ CoS_x was designed without the addition of CoS_x for comparison purposes and named 3DP-C/S. 3DP-C/S/ CoS_x cells, at a sulfur loading of 4 mg cm^{-2} and a current density of 1 mA cm^{-2} , delivered a high initial discharge capacity of $1891.7 \text{ mA h g}^{-1}$ and a reversible capacity of 1075 mA h g^{-1} after 100 cycles, corresponding to a capacity attenuation of $0.159\% \text{ cycle}^{-1}$. More importantly, at high sulfur loadings of 8 mg cm^{-2} and 3 mA cm^{-2} , we observed an initial discharge of $1118.8 \text{ mA h g}^{-1}$ and a capacity attenuation of 0.156% . The results herein indicate that the outlined dual-mechanism approach scales effectively for high sulfur loading cathodes and high current densities.

2. Results and Discussion

The route to realizing a channel-microarchitected 3DP-C/S/ CoS_x cathode can be broken down into four steps, as summarized in Figure 1. First, CoS_x was synthesized through a hydrothermal route. The composition and structure were observed by imaging the cathode under a scanning electron microscope (SEM) (Figure S1, Supporting Information). As shown in Figure S1 (Supporting Information), CoS_x nanoparticles can be successfully synthesized with a uniform size of 40–50 nm. The composition of CoS_x was found to be roughly 1:2.08, Co:S (at%), as found through energy-dispersive X-ray spectroscopy (EDX) and elemental mapping (Figure S3, Supporting Information). Second, two different cathodic inks were

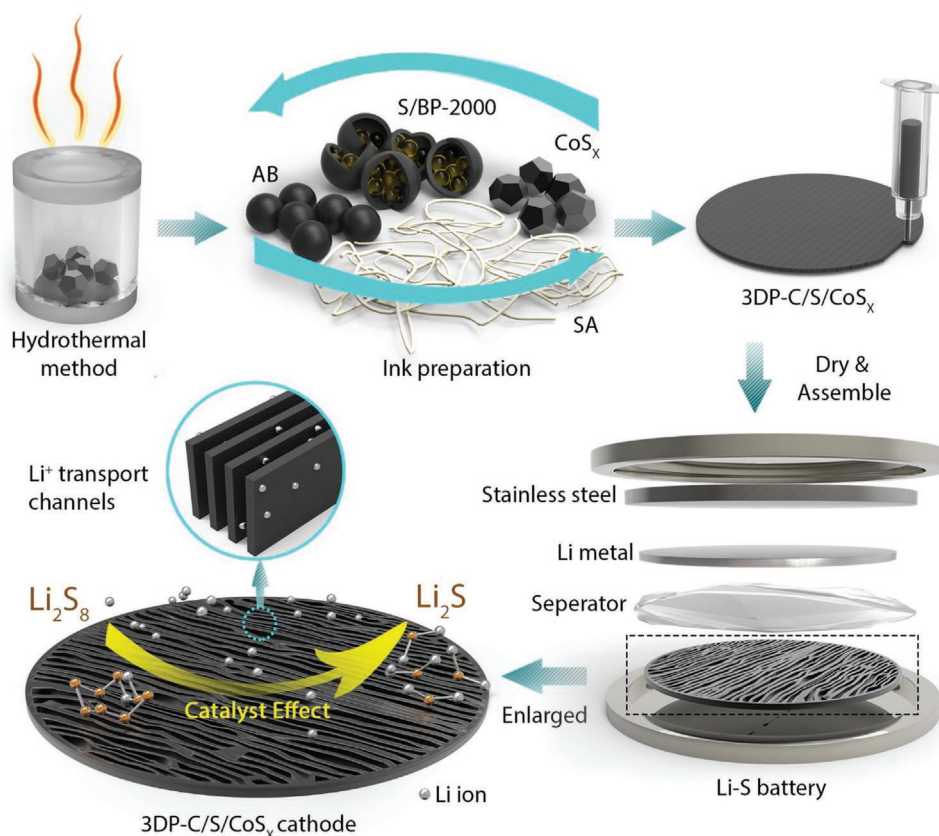


Figure 1. Schematic illustration of the 3DP-C/S/ CoS_x cathode synthesis and mechanisms of its advantages. AB: acetylene black; S/BP-2000: sulfur impregnated into a conductive carbon host (BP-2000); SA: sodium alginate.

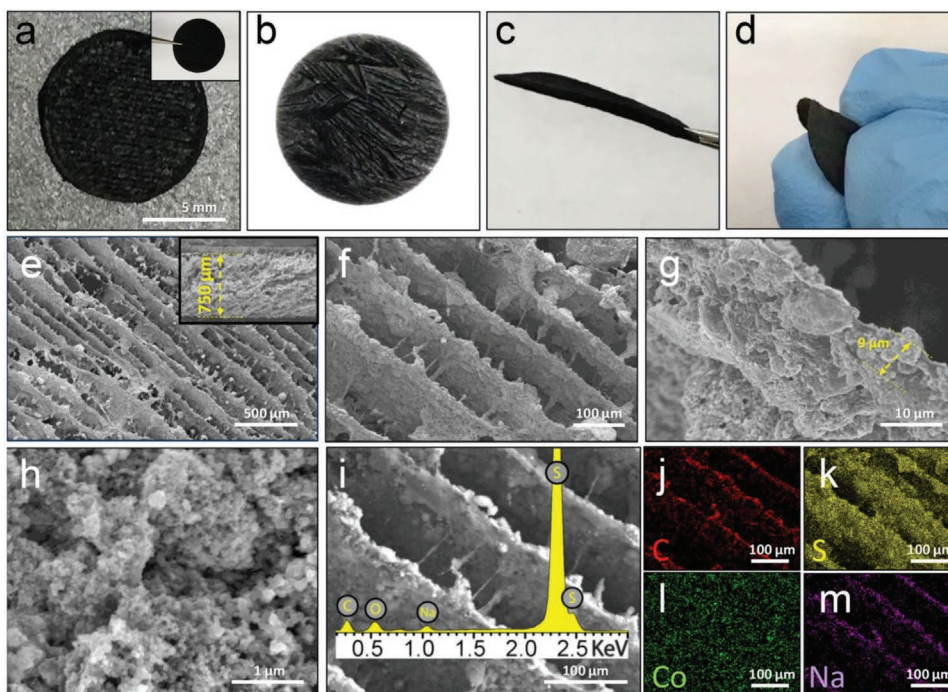


Figure 2. Optical images of 4 mg cm^{-2} 3DP-C/S/CoS_x, a) before and b–d) after freeze-drying. e–g) SEM images of 4 mg cm^{-2} 3DP-C/S/CoS_x under different magnifications with CoS_x, inset image: cross-sectional view. h) High-magnification SEM image of 3DP-C/S/CoS_x (4 mg cm^{-2} loading). j–m) Corresponding elemental mapping of C, S, Co, and Na from (i) with overlaid EDX.

prepared for testing: 3DP-C/S/CoS_x and 3DP-C/S. Both were prepared from a low-cost conductive carbon host, impregnated with 60% sulfur by weight, termed S/BP-2000 (Figure S4b, Supporting Information). The composition of S/BP-2000 was verified by thermogravimetric analysis (TGA) as demonstrated in Figure S5 (Supporting Information). Printable cathodic ink was prepared by mixing CoS_x (no CoS_x was added for 3DP-C/S), S/BP-2000, sodium alginate (SA), and acetylene black (AB) at a ratio of 8:1:1 (wt%). The third step was to print the ink into a 1 cm diameter circle with dense line patterns. The total thickness and areal loading of the electrode could be easily controlled by adjusting the number of printing layers. The fourth step was to freeze dry the as-printed cathode which induced the channel-like microarchitecture and sublimated the solvents.

Additive manufacturing, in conjunction with freeze-drying, developed multi-channeled surface microarchitecture (Figure 2a,b). The resulting 3DP-C/S/CoS_x cathode demonstrated good flexibility, as shown in Figure 2d, which promotes more surface area contact and better ion and electron transport.^[30] On the microscale, the channels formed were uniform, roughly 9–10 μm in width (Figure 2e–g). This process also uniformly distributed CoS_x on the printed cathode, as demonstrated by high-magnification imaging and EDX spectral mapping (Figure 2h–m) and confirmed by transmission electron microscopy (TEM) imaging (Figure S6, Supporting Information). As 3DP-C/S was also fabricated through an AM approach, it also had these physical features (Figure S7, Supporting Information).

Cyclic voltammetry (CV) tests were conducted by comparing 3DP-C/S/CoS_x to 3DP-C/S at a scan rate of 0.1 mV s^{-1} (Figure 3a). The two-step reduction of sulfur from S₈ to Li₂S_x

($X = 4–6$) and Li₂S_x to Li₂S₂/Li₂S is demonstrated in both cathode materials. The reduction is observed to be reversible by the anodic oxidation of Li₂S₂/Li₂S to S₈. Two details become apparent when comparing the cathodic and anodic peaks of 3DP-C/S and 3DP-C/S/CoS_x. First, there is a notably smaller difference in cathodic and anodic peaks for 3DP-C/S/CoS_x, compared to 3DP-C/S (0.3 vs 0.4 V). Second, 3DP-C/S/CoS_x's cathodic peaks at 2.0 and 2.3 V are far steeper than those of 3DP-C/S. These are both indicators of 3DP-C/S/CoS_x's faster sulfur redox kinetics and hence, more efficient sulfur utilization.^[31,32] This contribution was further investigated through an electrochemical impedance study (EIS). It is observable in the Nyquist plot of pre- and post-cycling that 3DP-C/S/CoS_x has a smaller charge-transfer resistance than 3DP-C/S, as revealed by the smaller semi-circle at high- to medium-frequency range (Figure S8, Supporting Information). As demonstrated in Figure 3b, 3DP-C/S/CoS_x and 3DP-C/S with a 4 mg cm^{-2} loading and a current density of 1 mA cm^{-2} delivered high initial discharge capacities of 1891.7 and 1052.9 mA h g⁻¹, respectively. Stable reversible capacities (seventh cycle) were measured at 1260.4 and 934.8 mA h g⁻¹ with discharge attenuations of 0.159% and 0.175% cycle⁻¹ (7th–100th cycle). The difference in performance can be attributed to the role of CoS_x. Figure 3c illustrates this distinction by observing the discharge/charge of the first cycle of 3DP-C/S/CoS_x and 3DP-C/S. The discharge curves also confirm the two-step reduction of sulfur through the appearance of two stable plateaus. The contribution of CoS_x to desirable electrochemical performance was further investigated through a comparative study of 3DP-C/S and 3DP-C/S/CoS_x with sulfur absent from the carbon host (details in the Experimental Section). The manufacturing and assembly steps

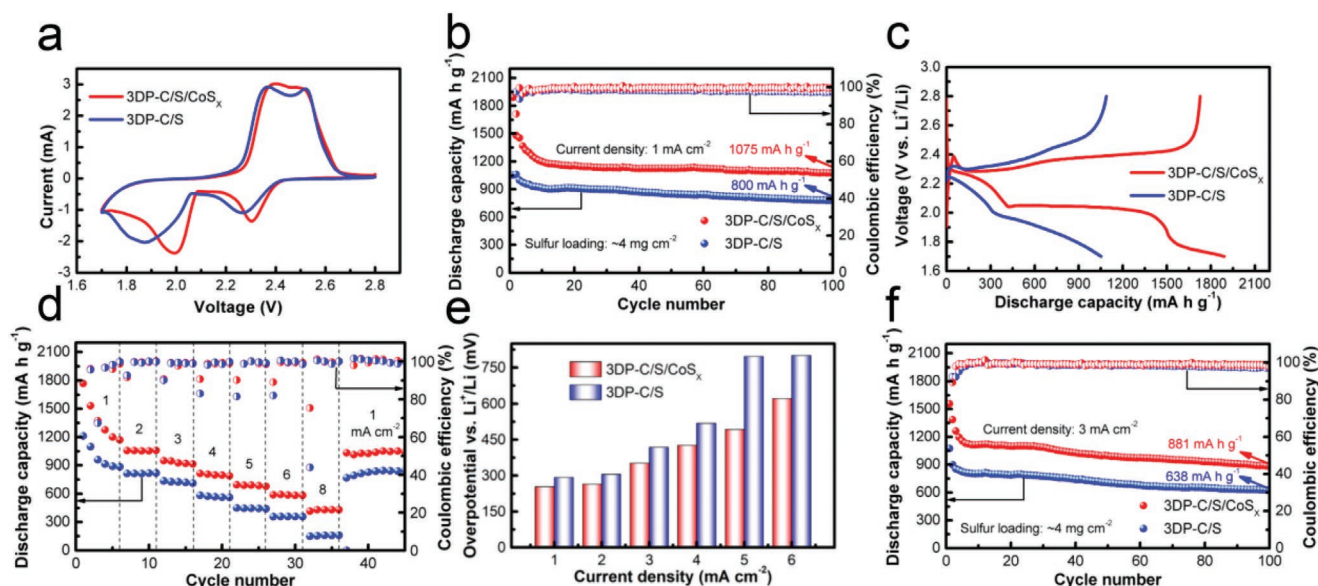


Figure 3. Comparison of electrochemical performances of 3DP-C/S/CoS_x and 3DP-C/S cathodes at sulfur loading of 4 mg cm⁻². a) CV profiles; b) cycling profiles at a current density of 1 mA cm⁻²; c) discharge/charge profiles for the initial cycle at 1 mA cm⁻²; d) rate profiles at different current densities from 1 to 8 mA cm⁻²; e) corresponding overpotential at different current densities; f) cycling profiles at a higher current density (3 mA cm⁻²).

of the cells were otherwise kept identical to those with sulfur. Sulfur-absent cells were tested under a 1 mA cm⁻² current density (Figure S9, Supporting Information). As expected, systems with the addition of CoS_x had a significantly higher charge/discharge capacity. At the initial cycle, the contribution of CoS_x to discharge capacity was 219.7 mA h g⁻¹ and after 100 cycles, 15.8 mA h g⁻¹. CoS_x's contribution of capacity to the overall cell is likewise clearly observed in Figure 3c.

To examine the electrode rate performance, C-rate tests of 3DP-C/S/CoS_x and 3DP-C/S were performed at current densities of 1, 2, 3, 4, 5, 6, and 8 mA cm⁻² and 4 mg cm⁻² loading (Figure 3d). The 3DP-C/S/CoS_x cells achieved stable cycling and average discharge capacities of 1384.5, 1055.5, 931.0, 801.0, 688.5, 587.8, and 428.3 mA h g⁻¹, respectively. When the current density was returned to 1 mA cm⁻², the capacity recovered to 1036.6 mA h g⁻¹. In comparison, the 3DP-C/S cells reached average discharge capacities of 992.9, 815.3, 723.7, 570.8, 445.9, 358.8, and 157.0 mA h g⁻¹ with a recovered capacity of 824.0 mA h g⁻¹. Electrodes as fabricated also exhibited good mechanical stability, as demonstrated by cycling tests (Figure S10a,c-f, Supporting Information). Cycling tests also show the cell separator of 3DP-C/S/CoS_x shifting from the clear hue of a pristine separator to light yellow (Figure S10b, Supporting Information). As LiPSs are characterized by dark yellow, the separator hue change indicates trapping of LiPSs at the cathode without excess dissolution into the electrolyte, which can improve cycling stability. Moreover, excellent cycling performance can be attributed to the thin channel-like microarchitecture as the channels helped promote favorable LiPS deposition mechanisms.^[33] In Figure S10c,d (Supporting Information), the pre-cycling images, compared to Figure S10e,f (Supporting Information), the post-cycling images, it is observable that LiPSs aggregated on the sides of the channels, thereby helping to maintain paths for ionic transport. As well, CoS_x was found to lower cell polarization, which agrees

well with reported literature.^[34] This is illustrated in Figure 3e, where it is evident that cells with CoS_x required notably lower overpotential to cycle. Moreover, under a higher current density of 3 mA cm⁻² and a sulfur loading of 4 mg cm⁻², 3DP-C/S/CoS_x and 3DP-C/S obtained initial discharge capacities of 1557.8 and 1073.9 mA h g⁻¹; stable reversible capacities of 1122.3 and 809.6 mA h g⁻¹; and discharge capacities of 881.3 and 622.1 mA h g⁻¹ after 100 cycles (Figure 3f).

To assess the performance of 3DP-C/S/CoS_x at and above expected commercial standards for Li-S batteries, high sulfur loading (6 and 8 mg cm⁻²) 3DP-C/S/CoS_x cells were assembled. As observable in Figures S11 and S12 (Supporting Information), the microarchitected channels were still reproducible at high sulfur loadings. Appropriate channel widths of ≈10 μm were maintained. Under 1 and 3 mA cm⁻² and a sulfur loading of 6 mg cm⁻², 3DP-C/S/CoS_x cells delivered an initial discharge of 1789.0 and 1396.7 mA h g⁻¹. After 100 cycles, the discharge capacity was 995.3 and 848.8 mA h g⁻¹ (Figure 4a). From the charge/discharge curves, the two-step reduction of LiPS (2.3, 2.1 V) is observable at all cycles via stable voltage plateaus (Figure 4b). To determine the stability and reversibility of high loading 3DP-C/S/CoS_x cells, a C-rate test was conducted with 6 mg cm⁻² 3DP-C/S/CoS_x at varying current densities (Figure 4c). Stable average discharge capacities were observed with a high recoverable discharge capacity at 1 mA cm⁻². Moreover, under a high sulfur loading of 8 mg cm⁻² and a 1 mA cm⁻² current density, 3DP-C/S/CoS_x was surprisingly able to deliver a high initial discharge capacity of 1593.6 mA h g⁻¹ (Figure S13, Supporting Information). The cell was also able to deliver a high specific capacity of 771.7 mA h g⁻¹ after 150 cycles at a 3 mA cm⁻² current density with an initial specific capacity of 1118.8 mA h g⁻¹ (Figure 4d). When compared to other reported high-loading Li-S cathodes, 3DP-C/S/CoS_x demonstrates both an exceptionally high areal capacity and initial discharge capacity (Figure S14 and Table S1, Supporting Information). A

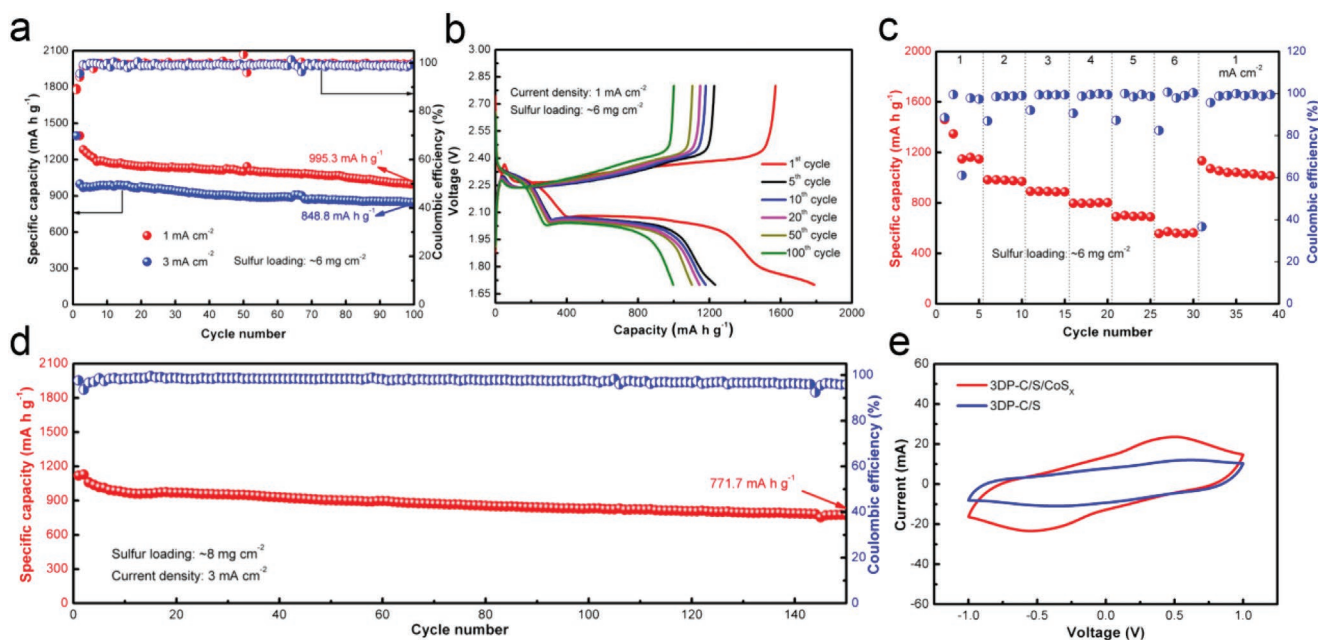


Figure 4. Electrochemical performances of high loading (6 and 8 mg cm⁻²) 3DP-C/S/CoS_x cathodes. a) Cycling profiles, b) charge/discharge profiles at select cycles, c) cycling profiles under different current densities from 1 to 6 mA cm⁻², d) cycling profile under 3 mA cm⁻², and e) CV plot comparing 3DP-C/S/CoS_x and 3DP-C/S in symmetric Li₂S₆-Li₂S₆ cells.

comparative CV test of symmetric Li₂S₆-Li₂S₆ cells with 3DP-C/S/CoS_x and 3DP-C/S was conducted to observe the catalyst effect of CoS_x, as shown in Figure 4e. The symmetric cell with 3DP-C/S/CoS_x delivered nearly two times higher current density than that of 3DP-C/S. This agrees with the previous electrochemical data in highlighting CoS_x's ability to boost electrochemical performance of the cell and with reported literature on the catalyst effect of cobalt sulfide in the Li-S battery system.^[19,35]

Another advantage of the reported electrode design is the ability for CoS_x to act as an adsorbent. The ability to promote the conversion of LiPSs (catalytic effect) and to trap LiPSs (adsorption) are two of the most promising mechanisms to prevent LiPS shuttling.^[36,37] This effect is schematically illustrated in Figure 5a. To investigate the capability for CoS_x to adsorb LiPSs, a visual-based static adsorption test was conducted. Sample tubes with pure CoS_x, a (10%) CoS_x/BP-2000 blend, pure BP-2000, and a reference tube were filled with Li₂S₆ and set aside for 5 h for static adsorption. As illustrated in Figure 5b, the hue differences between the post-adsorption samples were exceptionally clear. Samples with CoS_x (both pure and 10% CoS_x) showed a strong shift of hue from the dark yellow color of Li₂S₆ toward a clear, transparent solution. This greatly differed from the sample with only BP-2000, which displayed no obvious shift in hue. These stark differences reveal the effect CoS_x has in its affinity for and ability to trap LiPSs. X-ray absorption near edge structure (XANES) was conducted to verify the role of CoS_x as a catalyst for LiPS conversion and to confirm the observed adsorption effect. This was qualified by comparing the S K-edge and the Co K-edge of pristine CoS_x to CoS_x soaked in Li₂S₆/2-dimethoxymethane (DME) solution, abbreviated as CoS_x/Li₂S₆ (Figure 5c,d). As illustrated in Figure 5c, the Co pre-edge of CoS_x/Li₂S₆ samples demonstrated

a shift toward a lower energy level compared to the pristine CoS_x. This is an indication of partial Co reduction. The S K-edge (Figure 5d), illustrates a clear phenomenon of CoS_x/Li₂S₆ developing a strong S-S bond peak at ≈2472 eV.^[38] This peak is very weakly expressed in the pure CoS_x sample curve. This suggests that the peak developed due to contributions from the pure Li₂S₆ sample, which has a strong coincident S-S bond peak. Furthermore, the 2472 eV peak feature coincides with other reported sulfur features at the given energy level in sulfur-based elements and compounds (e.g., Li₂S_X (X = 4–8), elemental S, FeS₂).^[38] This suggests that Li₂S₆ was adsorbed by the CoS_x. From these two phenomena, and in conjunction with the visual adsorption tests, we found that CoS_x has both a strong adsorption effect and an affinity for Li₂S₆. This is ultimately reflected by 3DP-C/S/CoS_x's superior electrochemical performance compared to 3DP-C/S.

3. Conclusion

This work demonstrated a quick, low-cost approach to create a high sulfur loading cathode with great control over areal loading. Excellent electrochemical performance was obtained by leveraging both physical and chemical mechanisms to improve cycling stability and specific capacity. Additive manufactured electrodes were designed with channel-like micro-architecture which promoted fast ion transfer and favorable LiPS deposition sites. Cobalt sulfide was incorporated into the cathode composition and played two major roles: promoting LiPS adsorption and catalyzing the LiPS redox reaction. A cathode with this design, given 4 mg cm⁻² sulfur loading, delivered a high initial discharge of 1891.7 mA h g⁻¹ and a reversible capacity of 1075 mA h g⁻¹ after 100 cycles at current

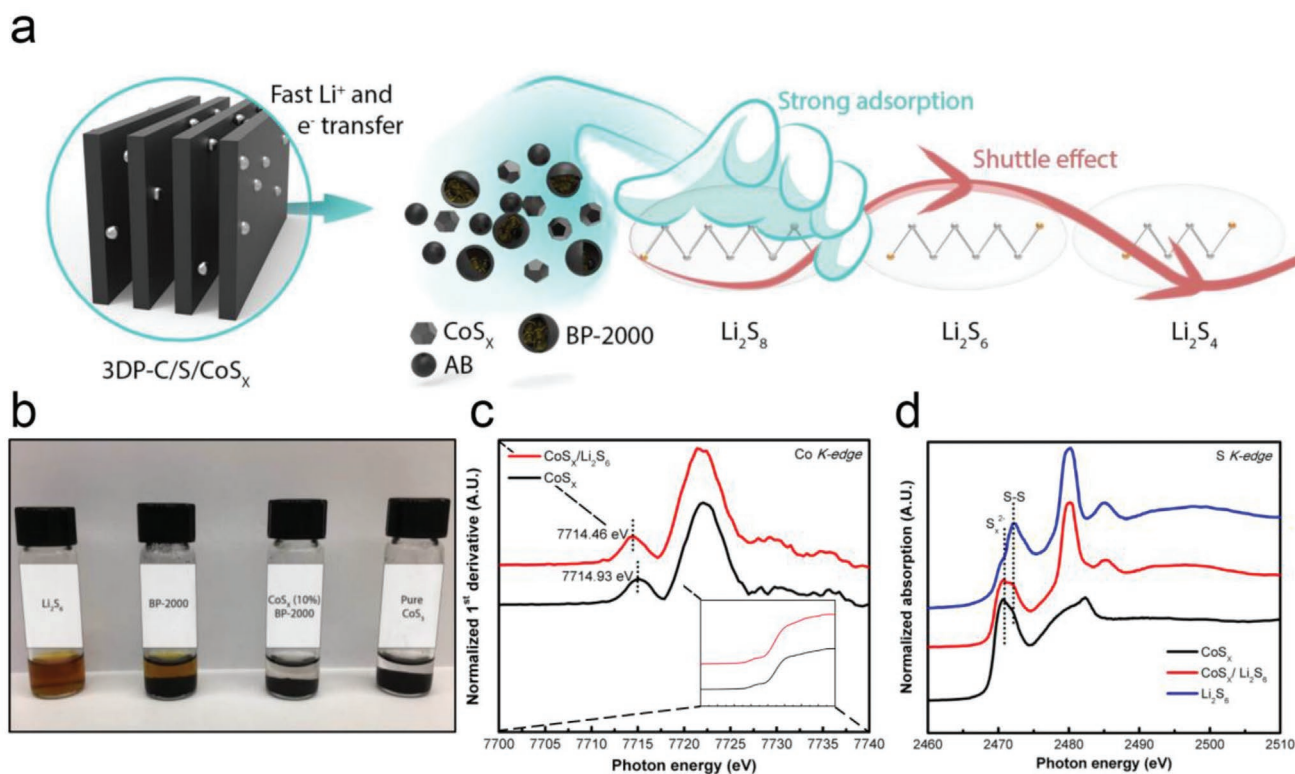


Figure 5. a) Schematic illustration of the adsorption of CoS_x in LiPS dissolution. b) Visual demonstration of static Li_2S_6 adsorption properties of carbon black (BP-2000), 3DP-C/S/ CoS_x , and CoS_x with pure Li_2S_6 as reference. c) First-order derivative of XANES cobalt K-edge; inset image: pre-edge region of normalized XANES cobalt K-edge. Axis and legends are the same. d) XANES sulfur K-edge.

density of 1 mA cm^{-2} . More significantly, at a high sulfur loading of 8 mg cm^{-2} , this cathode design delivered an initial discharge capacity of $1118.8 \text{ mA h g}^{-1}$ and reversible capacity of $771.7 \text{ mA h g}^{-1}$ after 150 cycles at current density of 3 mA cm^{-2} . This work outlines an effective route for synthesizing high sulfur loading cathodes. Furthermore, this work illustrates the effectiveness of combining innovation in both material selection and physical fabrication techniques to achieve high-performance Li-S cathodes.

4. Experimental Section

Synthesis of CoS_x : CoS_x (Figure S1, Supporting Information) was synthesized through a hydrothermal route. 0.03 M cobalt (II) nitrate hexahydrate was mixed with 0.3 M thioacetamide (98% purity), which acted as the source of sulfur, and $6.1 \times 10^{-5} \text{ M}$ polyvinylpyrrolidone (average MW $\approx 5.5 \times 10^4$) in a Teflon chamber filled anhydrous ethanol (30 mL). The solution was gently stirred by hand to ensure dispersion of solids into solution. The chamber was then loaded and sealed in a stainless-steel autoclave. The autoclave reactor was heated at $120 \text{ }^\circ\text{C}$ for 2.5 h and quenched in air. Amorphous CoS_x powder was obtained by filtering the solution through a $22 \text{ }\mu\text{m}$ diameter mesh filter paper and being dried at $60 \text{ }^\circ\text{C}$ (Figure S2, Supporting Information).

Synthesis of Sulfur into Carbon Host: Sulfur powder (99.98% pure) (Figure S4a, Supporting Information) was mixed with conductive carbon black (BP-2000) in a mortar at a 3:2 ratio by weight. The solids were crushed and mixed with a pestle for 20 min prior to transferring to an alumina crucible and sealed inside a stainless-steel reactor. The

mixture was heated at $155 \text{ }^\circ\text{C}$ for 8 h and at $300 \text{ }^\circ\text{C}$ for 4 h with change in temperature controlled at $5 \text{ }^\circ\text{C m}^{-1}$ (Figure S4b, Supporting Information). This process yielded a 60% sulfur powder, S/BP-2000, verified through thermogravimetric analysis (Figure S5, Supporting Information). Overall sulfur content in the 3DP-C/S/ CoS_x cells are 51.5% by weight.

Ink Preparation and Printing of Freestanding 3DP Cathodes: Printable ink was prepared in a two-step process: crushing and binding. CoS_x powder was crushed in a mortar and pestle by hand for 30 min to ensure particle uniformity and size ($\approx 10 \text{ }\mu\text{m}$). S/BP-2000 and porous AB were added to the mortar to form a (15% CoS_x , 85% S/BP-2000):AB ratio of 8:1 by weight. The solids were further mixed and crushed for 30 min. 2 wt% SA was added to form a final (15% CoS_x /S/BP-2000):AB:SA ratio of 8:1:1 by weight. Deionized water (1.5 mL) was dispersed in intervals of 0.5 mL followed by 3 min of mixing via pestle to obtain desired ink rheology. The final paste was loaded into a 3 cc syringe and attached to a Nordson EFD pneumatic fluid dispenser for semi-automatic deposition, paired with a tri-axis DeltaMaker 3D printer to control the printing path. A printing pressure of 20 PSI, ejection nozzle size of $150 \text{ }\mu\text{m}$, and printing speed of 6 mm s^{-1} were used. The structures were printed onto carbon paper, which acted as a temporary support. The printed cathodes were transferred to a $-15 \text{ }^\circ\text{C}$ refrigeration unit for 10 h after which the cathodes were freeze-dried in a freeze drier. The carbon paper support was then removed and discarded.

Adsorption Testing of CoS_x : Stock Li_2S_6 solution (0.5 M) was mixed with 3-dioxolane (DOL)/DME (1:1, v:v) at a ratio of 19:4 by volume, yielding a $0.5 \times 10^{-3} \text{ M}$ solution of Li_2S_6 . Three static adsorption samples were prepared in individual test tubes: CoS_x (45 mg), BP-2000 (45 mg), and BP-2000/ CoS_x (9:1, w:w, 45 mg). $5 \times 10^{-3} \text{ M}$ Li_2S_6 solution (1.1 mL) was added to each tube. A fourth sample tube was filled with pure $5 \times 10^{-3} \text{ M}$ Li_2S_6 as a reference. All steps were conducted under an argon atmosphere.

Materials Characterization: TGA was performed on an SDT Q600 analyzer under a nitrogen atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 25 to 600 $^{\circ}\text{C}$. Microarchitecture and morphology characterization of the cathode materials were carried out through imaging with a Hitachi S-4800 field emission scanning electron microscope (FESEM). EDX was conducted on the same FESEM. X-ray diffraction (XRD) was conducted on a Bruker D8 Advance. The XANES study was conducted on the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source (CLS) in Saskatoon. To preserve the purity, all samples that were transported to the CLS were sealed in Kapton tape and stored in a tape-sealed test tube, under an argon atmosphere.

Electrochemical Measurements: To evaluate the electrochemical performance, 3DP-C/S and 3DP-C/S/CoS_x cathodes were prepared and assembled in CR2032 coin cells with Li metal acting as the counter electrode.

Electrochemical performance of the 3DP-C/S and 3DP-C/S/CoS_x cathodes was assembled and tested in CR2032 coin cells, with assembly conducted in a sealed, argon-filled glove box. Lithium metal was used as the anode, and two layers of polypropylene wafers (Celguard 2400) were used as the separator. The electrolyte used was a 1 m bis(trifluoromethylsulfonyl) imide (LiTFSI) in DME/DOL (1:1, v:v) with 1 wt% LiNO₃ salt additive. For cells with sulfur loading under 3 mg cm^{-2} , 20 μL of electrolyte was used. For cells between 3 and 6 mg cm^{-2} sulfur loading, 40 μL of electrolyte was used. For cells with sulfur loading exceeding 6 mg cm^{-2} , between 50 and 60 μL of electrolyte was used.

EIS was conducted on an open circuit with a frequency range of 5.0×10^5 to 1.0×10^{-2} Hz on a multichannel potentiostat (VMP, BioLogic). Charge/discharge testing was conducted on a LAND CT-2001A system with voltage controlled between 1.7 and 2.8 V at 25 $^{\circ}\text{C}$. Unless specified, all reported capacities in this work are based on sulfur, and the reported voltages are in respect to Li⁺/Li (vs Li⁺/Li).

Symmetric Cell Tests: Symmetric Li₂S₆-Li₂S₆ cells were assembled and tested in CR2303 coin cells. Assembly was conducted in a sealed, argon-filled glove box. 0.5×10^{-3} M Li₂S₆ was prepared by diluting 0.5 M stock Li₂S₆ with 1 M LiTFSI dissolved in DOL/DME (1:1, v:v).

CoS_x Catalytic Contribution Tests: "No-sulfur" cathodes were prepared by the same procedure as 3DP-C/S and 3DP-C/S/CoS_x cathodes; however, BP-2000 and acetylene black were mixed at an 8:1 mass ratio and used in place of S/BP-2000 in the previously outlined methodology.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

3D printing, cobalt sulfide catalyst, high sulfur loading, Li-S cathode

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- [1] H. J. Peng, J. Q. Huang, Q. Zhang, *Chem. Soc. Rev.* **2017**, *46*, 5237.
- [2] E. Umeshbabu, B. Zheng, Y. Yang, *Electrochem. Energy Rev.* **2019**, *2*, 199.
- [3] L. Li, X. Zhang, M. Li, R. Chen, F. Wu, K. Amine, J. Lu, *Electrochem. Energy Rev.* **2018**, *1*, 461.
- [4] H.-J. Peng, J.-Q. Huang, X.-B. Cheng, Q. Zhang, *Adv. Energy Mater.* **2017**, *7*, 1700260.
- [5] Z. W. Seh, Y. Sun, Q. Zhang, Y. Cui, *Chem. Soc. Rev.* **2016**, *45*, 5605.
- [6] X. Liu, J.-Q. Huang, Q. Zhang, L. Mai, *Adv. Mater.* **2017**, *29*, 1601759.
- [7] X. Ji, K. T. Lee, L. Nazar, *Nat. Mater.* **2009**, *8*, 500.
- [8] X. Yang, X. Li, K. Adair, H. Zhang, X. Sun, *Electrochem. Energy Rev.* **2018**, *1*, 239.
- [9] A. Rosenman, E. Markevich, G. Salitra, D. Aurbach, A. Garsuch, F. F. Chesneau, *Adv. Energy Mater.* **2015**, *5*, 1500212.
- [10] X. Fang, H. S. Peng, *Small* **2015**, *11*, 1488.
- [11] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* **2012**, *11*, 19.
- [12] W. Chen, T. Qian, J. Xiong, N. Xu, X. Liu, J. Liu, J. Zhou, X. Shen, T. Yang, Y. Chen, C. Yan, *Adv. Mater.* **2017**, *29*, 1605160.
- [13] X. Li, X. Sun, *Adv. Funct. Mater.* **2018**, *28*, 1801323.
- [14] X. Li, J. Liang, J. Luo, C. Wang, X. Li, Q. Sun, R. Li, L. Zhang, R. Yang, S. Lu, H. Huang, X. Sun, *Adv. Mater.* **2019**, *31*, 1808100.
- [15] S. Wang, H. Chen, J. Liao, Q. Sun, F. Zhao, J. Luo, X. Lin, X. Niu, M. Wu, R. Li, X. Sun, *ACS Energy Lett.* **2019**, *4*, 755.
- [16] L. Ma, K. E. Hendrickson, S. Wei, L. A. Archer, *Nano Today* **2015**, *10*, 315.
- [17] A. Manthiram, Y. Fu, Y.-S. Su, *Acc. Chem. Res.* **2013**, *46*, 1125.
- [18] D. Liu, C. Zhang, G. Zhou, W. Lv, G. Ling, L. Zhi, Q.-H. Yang, *Adv. Sci.* **2018**, *5*, 1700270.
- [19] X. Yang, X. Gao, Q. Sun, S. Jand, Y. Yu, Y. Zhao, X. Li, K. Adair, L.-Y. Kuo, J. Rohrer, J. Liang, X. Lin, M. N. Banis, Y. Hu, H. Zhang, X. Li, R. Li, H. Zhang, P. Kaghazchi, T.-K. Sham, X. Sun, *Adv. Mater.* **2019**, *31*, 1901220.
- [20] Z. Yuan, H. Peng, T. Hou, J. Huang, C. Chen, D. Wang, X. Cheng, F. Wei, Q. Zhang, *Nano Lett.* **2016**, *16*, 519.
- [21] Y. Sun, C. Liu, D. C. Grauer, J. Yano, J. Long, P. Yang, C. Chang, *J. Am. Chem. Soc.* **2013**, *135*, 17699.
- [22] X. Gao, Q. Sun, X. Yang, J. Liang, A. Koo, W. Li, J. Liang, J. Wang, R. Li, F. Holness, A. Price, S. Yang, T.-K. Sham, X. Sun, *Nano Energy* **2019**, *56*, 595.
- [23] J. Cai, Z. Fan, J. Jin, Z. Shi, S. Dou, J. Sun, Z. Liu, *Nano Energy* **2020**, *75*, 104970.
- [24] J. Cai, J. Jin, Z. Fan, C. Li, Z. Shi, J. Sun, Z. Liu, *Adv. Mater.* **2020**, *32*, 2005967.
- [25] X. Tian, J. Jin, S. Yuan, C. Chua, S. Tor, K. Zhou, *Adv. Energy Mater.* **2017**, *7*, 1700127.
- [26] Y. Wang, D. Kong, W. Shi, B. Liu, G. Sim, Q. Ge, H. Yang, *Adv. Energy Mater.* **2016**, *6*, 1601057.
- [27] X. Yang, Y. Chen, M. Wang, H. Zhang, X. Li, H. Zhang, *Adv. Funct. Mater.* **2016**, *26*, 8427.
- [28] S. Rehman, K. Khan, Y. Zhao, Y. Hou, *J. Mater. Chem. A* **2017**, *5*, 3014.
- [29] J. Gao, H. Abruna, *J. Phys. Chem. Lett.* **2014**, *5*, 882.

- [30] X. Lu, H. Dou, B. Gao, C. Yuan, S. Yang, L. Hao, L. Shen, X. Zhang, *Electrochim. Acta* **2011**, *56*, 5115.
- [31] X. Liang, C. Kwok, F. Lodi-Marzano, Q. Pang, M. Cuisinier, H. Huang, C. Hart, D. Houtarde, K. Kaup, H. Sommer, T. Brezesinski, J. Janek, L. Nazar, *Adv. Energy Mater.* **2016**, *6*, 1501636.
- [32] S. Zhang, *J. Electrochem. Soc.* **2012**, *159*, A920.
- [33] F. Fan, W. Carter, Y.-M. Chiang, *Adv. Mater.* **2015**, *27*, 5203.
- [34] P. Zuo, J. Hua, M. He, H. Zhang, Z. Qian, Y. Ma, C. Du, X. Cheng, Y. Gao, G. Yin, *J. Mater. Chem. A* **2017**, *5*, 10936.
- [35] X. Gao, X. Yang, M. Li, Q. Sun, J. Liang, J. Luo, J. Wang, W. Li, J. Liang, Y. Liu, S. Wang, Y. Hu, Q. Xiao, R. Li, T.-K. Sham, X. Sun, *Adv. Funct. Mater.* **2019**, *29*, 1806724.
- [36] G. Zhou, H. Tian, Y. Jin, X. Tao, B. Liu, R. Zhang, Z. Seh, D. Zhuo, Y. Liu, J. Sun, J. Zhao, C. Zu, D. Wu, Q. Zhang, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 840.
- [37] J. Park, B.-C. Yu, J. S. Park, J. Choi, C. Kim, Y.-E. Sung, J. Goodenough, *Adv. Energy Mater.* **2017**, *7*, 1602567.
- [38] M. Patel, I. Arcon, G. Aquilanti, L. Stievano, G. Mali, R. Dominko, *ChemPhysChem* **2014**, *15*, 894.