Co₃O₄-Carbon Cloth free standing cathode for lithium sulfur battery

Jing Xu, Dawei Su, Guoxiu Wang*
Centre for Clean Energy Technology, University of Technology Sydney, NSW 2007, Australia.

*E-mail: Jing. Xu@student.uts.edu.au

Abstract. Lithium–sulfur (Li–S) battery has been considered to be one of the most promising next-generation electrochemical energy-storage systems due to its high theoretical energy of 2600 Wh kg⁻¹ with low cost. The insulating nature of both sulfur and the dissolution of polysulfides are the two primary challenges for the application of lithium sulfur batteries. Here, we developed a binder-free cathode by chemisorption of Co₃O₄ to carbon cloth (CC), which was used as a 3D current collector to accommodate a large amount of sulfur, multiwall carbon nanofiber (MWCNF) and carbon black (CB) hybrids within the conductive scaffold, enabling the fabrication of ultrahigh sulfur loaded electrodes. The interconnected carbon fibers established a long-range conductive matrix for an efficient electron transport, the multiple conductive pathways guarantee high sulfur utilization. More importantly, the high electrolyte absorbability of the Co₃O₄-CC-S current collector facilitates well-localized polysulfides within the Co₃O₄-CC-S, meanwhile, the polar Co₃O₄ could also effectively entrapped the intermediated polysulfides preventing their free diffusion to the lithium anode, guaranteeing good cycling stability. Consequently, the Co₃O₄-CC-S electrodes exhibit excellent electrochemical performance with sulfur loading of 4.3 mg cm⁻².

1. Introduction
We significantly stabilized cycle life of high sulfur loading binder-free cathode by chemisorption of Co₃O₄ to carbon fiber cloth, which was used as a 3D current collector to accommodate a large amount of sulfur, MWCNF and CB hybrids within the conductive scaffold, enabling the fabrication of ultrahigh sulfur loaded electrodes.¹² This special nanoarchitecture combines the advantage of strong chemisorption of lithium polysulfides as well as excellent electrical conductivity, enabling high sulfur utilization and effective trap of lithium polysulfides. When applied as cathode materials for lithium sulfur batteries, the cathodes exhibit a reversible capacity of 1007 mAh g⁻¹ after 300 cycles.

2. Experiment
Firstly, Co₃O₄ nanocages were constructed on carbon cloth (CC) by a solvothermal method. In a typical procedure, 0.1 of poly(vinylpyrrolidone) (PVP, Mw = 360000 g mol⁻¹, 99 %) was well dispersed in 7.5 ml of deionized water and 7.5 ml of ethanol (95 %) by stirring treatment, then 0.5 mmol of Co(NO₃)₂•6H₂O (> 98%) were dissolved into the above dispersion by continuous stirring for 30 min. CC which was pre-treated by an acid treatment were performed to functionalize CC with oxygen containing groups. Pristine CC were cut into circular disks with a diameter of 1.4 cm and soaked in HNO₃ solution at 60 °C for 3 h. Acid-treated CC were then washed by water and dried at 60 °C for 24 h. Then transform the as-made solution and CC into a 25 ml
Teflon-Lined stainless steel autoclave and reacted at 180 °C for 12 h. When the reaction finished, the solution was cooled down to room temperature naturally and washed to obtain the black Co₃O₄-CC. Then heated at 450 °C for 1 h under N₂ atmosphere. Homogeneous sulfur-containing slurry was fabricated by mixing 90 wt% sulfur, 5 wt% carbon black, and 5 wt% MWCNFs in N-methyl-2-pyrrolidone (NMP) followed by high power ultrasonication for 0.5 h. The as-prepared Co₃O₄-CC was immersed into the slurry for 10 min, then the Co₃O₄-CC was removed from the slurry and placed in a vacuum oven at 60 °C overnight to obtain the Co₃O₄-CC-S electrode.

3. Results

![Scheme 1](image)

**Scheme 1.** Schematic illustration for the formation of Co3O4-CC-S.

By using our simple method, an activated carbon cloth was used as a template for the preparation of Co₃O₄-CC-S composite (Scheme 1). Co₃O₄ particles were successfully coated on the surface of CFCs. The as-prepared Co₃O₄ characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 1b, the as-made Co₃O₄ exhibits regular nanocubic morphology and has a uniform particle size of approximate 400 nm, also the surface of Co₃O₄ was smooth, which was consistent with the TEM result in Figure 1f, the surface of which shows high crystallinity without any detectable by-products as revealed by the X-ray diffraction pattern (Figure 2b). The structure of the Co₃O₄-CC-S was characterized by scanning electron microscopy (SEM) in Figure 1, it can be seen that sufficient void space, tens of micrometers in size, was generated by the randomly interconnected carbon fibers, which is capable of holding a large amount of active material, maintaining high electrolyte absorbability and effectively accommodating the volume expansion of sulfur during discharge.

The Co₃O₄-CC-S electrodes were prepared by immersing the Co₃O₄-CC in a premixed sulfur slurry containing 70 wt% commercial pure sulfur powder, 10 wt% carbon black(CB), and 20 wt% MWCNFs after high-power ultrasonication, it needs to be pointed out that MWCNFs were used in the sulfur slurry instead of conventional polymeric binders in integrated binder-free electrodes. From the X-ray diffraction pattern of the Co₃O₄-CC-S shown in Figure 2b, it can be seen that all the diffraction peaks are well indexed as sulfur structure, indicating that sulfur was successfully encapsulated into the porous structure. This seems to be further supported by the Raman spectroscopy analysis. In Figure 2c, we can detect distinct sulfur peaks at around 200 cm⁻¹, confirming that sulfur effectively diffuse into the Co₃O₄-CC composites. The 3D Co₃O₄-CC skelton is capable of holding a high, uniformly distributed concentration of the active material within its interconnected pores, enabling a high sulfur loading. We also characterized the structure of the sulfur-MWCNF-CB clusters loaded on the Co₃O₄-CC, considering the distribution of sulfur is closely associated with the electrochemical performance of the electrode. It was seen that the MWCNFs and CB are not simply surrounded around the sulfur particles, but homogeneously dispersed through the sulfur and formed an interconnected and embedded conductive network, the corresponding elemental maps of carbon and sulfur revealing that sulfur is uniformly distributed within the carbon conductive network constructed by MWCNFs and CB. In this work, we demonstrate that an embedded conductive scaffold formed by MWCNFs and CB can be constructed through the insulated sulfur, which is highly desirable for high sulfur utilization during the electrochemical redox process.
Electrochemical measurements were conducted to compare the performance of Co$_3$O$_4$-CC-S and CC/S. Both the sulfur mass loading and the amount of electrolyte added in the coin cells were kept at the same level for Co$_3$O$_4$-CC-S and CC-S composites. Figure 3a, b illustrate the charge/discharge profiles of Co$_3$O$_4$-CC-S and CC/S in the first, second and 300th cycles, it is noteworthy that Co$_3$O$_4$-CC-S exhibits higher first-discharge plateau at around 2.37 V and wider second-discharge plateau at around 2.1 V compared with pure CNF/S electrodes, and even after 300 cycles, the discharge plateau still remain well, indicating more sulfur utilization in the Co$_3$O$_4$-CC-S. The cycling performance and Coulombic efficiency of the Co$_3$O$_4$-CC-S composite and pure CC-S electrodes over long-term cycles are shown in Figure 3d. After 300 cycles, the reversible capacity of Co$_3$O$_4$-CC-S is around 1007 mAh g$^{-1}$, the capacity retained 81% of the initial capacity after 300 cycles at 0.5C, while the stability of pure CNF/S electrode is significantly lower than that of Co$_3$O$_4$-CC-S, the capacity degraded to merely 434 mAh g$^{-1}$ by 300th cycles. We also cycled the Co$_3$O$_4$-CC-S electrodes at different current rates. Figure 3c shows the results of Co$_3$O$_4$-CC-S and CC-S electrode cycled at step-wise current rates. During the discharge-charge process, the electrodes were consecutively cycled at 0.1C, 0.5C, 1C, 2C, 3C and then reversed back to low rates. It should be noted that when the current reversed back to 0.1C, the Co$_3$O$_4$-CC-S electrode could retain a capacity of 950 mAh g$^{-1}$, while the figure for CC-S electrodes was only 370 mAh g$^{-1}$.

**Figure 1.** (a, b)SEM image of Co$_3$O$_4$-CC. (c)Mapping results of Co$_3$O$_4$-CC-S. (d)SEM image of Co$_3$O$_4$-CC-S. (e)TEM image of Co$_3$O$_4$. (f) SAED pattern for Co$_3$O$_4$. 

Electrochemical measurements were conducted to compare the performance of Co$_3$O$_4$-CC-S and CC/S. Both the sulfur mass loading and the amount of electrolyte added in the coin cells were kept at the same level for Co$_3$O$_4$-CC-S and CC-S composites. Figure 3a, b illustrate the charge/discharge profiles of Co$_3$O$_4$-CC-S and CC/S in the first, second and 300th cycles, it is noteworthy that Co$_3$O$_4$-CC-S exhibits higher first-discharge plateau at around 2.37 V and wider second-discharge plateau at around 2.1 V compared with pure CNF/S electrodes, and even after 300 cycles, the discharge plateau still remain well, indicating more sulfur utilization in the Co$_3$O$_4$-CC-S. The cycling performance and Coulombic efficiency of the Co$_3$O$_4$-CC-S composite and pure CC-S electrodes over long-term cycles are shown in Figure 3d. After 300 cycles, the reversible capacity of Co$_3$O$_4$-CC-S is around 1007 mAh g$^{-1}$, the capacity retained 81% of the initial capacity after 300 cycles at 0.5C, while the stability of pure CNF/S electrode is significantly lower than that of Co$_3$O$_4$-CC-S, the capacity degraded to merely 434 mAh g$^{-1}$ by 300th cycles. We also cycled the Co$_3$O$_4$-CC-S electrodes at different current rates. Figure 3c shows the results of Co$_3$O$_4$-CC-S and CC-S electrode cycled at step-wise current rates. During the discharge-charge process, the electrodes were consecutively cycled at 0.1C, 0.5C, 1C, 2C, 3C and then reversed back to low rates. It should be noted that when the current reversed back to 0.1C, the Co$_3$O$_4$-CC-S electrode could retain a capacity of 950 mAh g$^{-1}$, while the figure for CC-S electrodes was only 370 mAh g$^{-1}$.
Figure 2. TGA curve(a), XRD patterns (b) and Raman spectra (c) of Co$_3$O$_4$-CC-S
Figure 3. (a) Galvanostatic charge and discharge profiles of Co$_3$O$_4$-CC-S for different cycles at 0.2C.
(b) Galvanostatic charge and discharge profiles of CC-S for different cycles at 0.2C.
(c) Discharge/Charge capacity cycled at various rates from 0.1 C, 0.5 C, 1 C, 2 C, 5 C.
(d) Long term cycling performance test of the Co$_3$O$_4$-CC-S, CC-S electrodes at 0.2C discharge rate and corresponding Coulombic efficiency.

4. Discussion
The interaction of different sulfur host materials (CC, Co$_3$O$_4$-CC) with lithium polysulfides were probed by visual discrimination, taking Li$_2$S$_6$ as the representative polysulfide. An equivalent amount of host materials were first added to Li$_2$S$_6$ solution. The superior intrinsic capability of Co$_3$O$_4$-CC to absorb Li$_2$S$_6$ was clearly obvious, as shown in Figure 4. The adding of Co$_3$O$_4$-CC rendered the Li$_2$S$_6$ solution light yellow after resting for 3h, implying strong adsorption while the carbon black solution did not exhibit obvious change, indicative of no interaction. Hence, the results from the visible experiment are highly consistent with the cycling performance of the batteries and further confirm the strong capability of Co$_3$O$_4$-CC-S in confining the LiPS species.

Figure 4. (a) Initially mixed. (b) Aging for 3h. ((1)Li$_2$S$_6$ solution. (2)CC-S adding into Li$_2$S$_6$ solution. (3) Co$_3$O$_4$-CC adding into Li$_2$S$_6$ solution.)
5. Conclusion
In summary, we designed a binder-free cathode by chemisorption of Co$_3$O$_4$ to carbon fiber cloth, and applied this as a 3D current collector to accommodate a large amount of sulfur, multiwall carbon nanofiber (MWCNF) and carbon black (CB) hybrids within the conductive scaffold. The electrode with a high sulfur loading exhibits low polarization, stable cycling performance, and excellent rate capability compared with pure CC-S cathodes. The excellent performance could be attributed to synergic effects, including the high surface area and high conductivity of the CC-S matrix, as well as the strong polysulfides binding capability of Co$_3$O$_4$ particles. Moreover, Co$_3$O$_4$ nanocrystals probably participate in multiple polysulfide transformation, affecting the redox reaction environment favourably, leading to the improvement in the reversibility of Li$_2$S/polysulfides/S conversion. When applied as cathode material for lithium sulfur batteries, it exhibits superior cycling performance and excellent rate capability. This work opens a new opportunity for the realization of high-energy and commercially viable Li-S batteries.

References
[1] Fang R, Zhao S, Sun Z, Wang DW, Cheng HM, Li F. More Reliable Lithium-Sulfur Batteries: Status, Solutions and Prospects. Advanced materials, 2017.
[2] Wang J-G, Xie K, Wei B. Advanced engineering of nanostructured carbons for lithium–sulfur batteries. Nano Energy 15, 2015.