Development of Novel Nanomaterials for Lithium Sulfur Batteries

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Abstract

Lithium-sulfur batteries are considered as the most promising next generation high-energy batteries. Compared with other kinds of battery, Li-S batteries have ultra-high theoretical energy density, which is a good candidate for electric vehicles and hybrid electric vehicles in future. However, there are still many challenges to be addressed in Li-S batteries. Design of electrodes, selection of electrolytes, and battery assemble have direct effects on the safety, cost and electrochemical performance of Li-S batteries. Therefore, it is greatly important to develop novel electrodes to achieve high-energy for Li-S batteries. This thesis mainly focuses on the design of sulfur cathode of Li-S batteries and mainly include six parts.

The first part in the thesis investigated effects of carbon-heteroatom bonds on sulfur cathode. A series of carbon black substrates were prepared using various treatments to introduce nitrogen or oxygen surface species. The results indicated that nitrogen-doped carbon black significantly improved the electrochemical performance of sulfur cathode materials. Synchrotron-based XPS revealed that the defect sites of nitrogen-doped carbon are favorable for the discharge product deposition, leading to a high utilization and reversibility of sulfur cathodes. The studies also found that the introduction of oxygen functional groups results in deteriorated performance of Li–sulfur batteries due to the reduced conductivity and unwanted side reactions occurring between sulfur and surface oxygen species.

To further improve the performance of sulfur cathodes, titanium nitride decorated carbon materials were designed and synthesized as carbon host in the second part of the thesis. TiN nanoparticles were synthesized via atomic layer deposition, which are uniformly distributed on porous carbon with small particle size. Electrochemical results indicated that as-prepared TiN@carbon facilitates the rate performance of sulfur cathodes, which demonstrated an improved cyclic capability and stability of Li-S batteries.

The third part of the thesis is application of metal organic framework derived carbon (MOF-C) with controllable porous structure for sulfur cathodes. The in-situ ammonia treatment successfully prepared MOF-C with different porous structure. Further, NH₃ treated MOF-C as carbon host for sulfur loading performing as the cathode for Li–S batteries resulted in twice higher capacity retention than that of pristine MOF-C. Further, different Li–S electrochemical
mechanisms regarding the different porous structures of carbon were also revealed and investigated in this part.

Apart from development of different carbon materials for sulfur cathodes, coating material is another popular strategy to improve the performance of sulfur cathodes. The fourth part of the thesis introduced atomic layer deposited $\text{Al}_2\text{O}_3$ coating to prevent dissolution of polysulfide for sulfur cathodes. It was demonstrated that the $\text{Al}_2\text{O}_3$ coating significantly improved the cycling stability of Li–sulfur batteries. The underlying mechanism by synchrotron-based X-ray photoelectron spectroscopy was investigated.

To further improve coating materials for sulfur cathode, molecular layer deposited alucone coating was developed for sulfur electrode in the fifth part of the thesis. The alucone coated C/S cathode displayed over two-times higher discharge capacity than the pristine one, demonstrating a greatly prolonged cycle life. Morphology of discharge product after cycling was also investigated in this part to understand the mechanism of alucone coating.

Safety is a crucial concern for Li-S batteries. The sixth part of the thesis was to develop safe and durable high temperature Li-S batteries. The commonly employed ether-based electrolyte does not enable to realize safe Li–S batteries operated at high-temperature due to the low boiling and flash temperatures of ether-based electrolyte. Traditional carbonate-based electrolyte can obtain safe physical properties at high temperature for Li ion batteries but cannot complete reversible electrochemical reaction for most Li-S batteries. By using molecular layer deposition (MLD), sulfur cathodes with alucone coating can complete the reversible electrochemical process in carbonate electrolyte and exhibit a safe and ultra-stable cycle life at high temperature. Synchrotron-based X-ray analysis was carried out to understand the mechanism of alucone coating in Li-S batteries.

**Keywords**

Lithium sulfur batteries, high energy density, sulfur cathode, carbonate-based electrolyte, ether-based electrolyte, carbon hosts, heteroatoms-doped carbon, gas phase treatment, metal organic framework derived carbon, atomic layer deposition, molecular layer deposition, high temperature Li-S batteries, safety, synchrotron radiation, XPS, XAS, XANES.
Co-Authorship Statement

1.

**Title**: Nitrogen-doped carbons in Li–S batteries: materials design and electrochemical mechanism

**Authors**: Xia Li and Xueliang Sun

The final version of this manuscript has been published in Frontiers in Energy Research, 2014, 2, 49. All the authors contributed to designing, writing, and modifying the manuscript.

2.

**Title**: Tailoring interactions of carbon and sulfur in Li–S battery cathodes: significant effects of carbon–heteroatom bonds

**Authors**: Xia Li, Xifei Li, Mohammad N. Banis, Biqiong Wang, Andrew Lushington, Xiaoyu Cui, Ruying Li, Tsun-Kong Sham, and Xueliang Sun

The final version of this manuscript has been published in Journal of Materials Chemistry A, 2014, 2, 12866. Xifei Li conducted the measurement of surface area. Mohammad N. Banis, Biqiong Wang, Xiaoyu Cui, and Tsun-Kong Sham conducted synchrotron based X-ray tests; Ruying Li provided access to the equipment. Andrew Lushington contributed editorial comments on the manuscript.

3.

**Title**: Nanoscale stabilization of Li–sulfur batteries by atomic layer deposited Al_2O_3

**Authors**: Xia Li, Jian Liu, Biqiong Wang, Mohammad N. Banis, Biwei Xiao, Ruying Li, Tsun-Kong Sham, and Xueliang Sun

The final version of this manuscript has been published in RSC Advances, 2014, 4, 27126. Jian Liu conducted ALD experiments. Biqiong Wang, Mohammad N. Banis, and Tsun-Kong Sham conducted synchrotron based X-ray tests; Ruying Li provided access to the equipment. All authors contributed editorial comments on the manuscript.
4.  

**Title:** Superior stable sulfur cathodes of Li–S batteries enabled by molecular layer deposition  

**Authors:** Xia Li, Andrew Lushington, Jian Liu, Ruying Li, and Xueliang Sun  

The final version of this manuscript has been published in *Chemical Communications*, 2014, 4, 27126. Andrew Lushington and Jian Liu conducted MLD experiments. Ruying Li provided access to the equipment. All authors contributed editorial comments on the manuscript.  

5.  

**Title:** Tunable porous structure of metal organic framework derived carbon and the application in lithium sulfur batteries  

**Authors:** Xia Li, Qian Sun, Jian Liu, Biwei Xiao, Ruying Li, and Xueliang Sun  

The final version of this manuscript has been published in *Journal of Power Sources*, 2016, 302, 174. Qian Sun and Biwei Xiao conducted Raman experiments. Ruying Li provided access to the equipment. All authors contributed editorial comments on the manuscript.  

6.  

**Title:** Safe and Durable High-Temperature Lithium–Sulfur Batteries via Molecular Layer Deposited Coating  

**Authors:** Xia Li, Andrew Lushington, Qian Sun, Wei Xiao, Jian Liu, Biqiong Wang, Yifan Ye, Kaiqi Nie, Yongfeng Hu, Qunfeng Xiao, Ruying Li, Jinghua Guo, Tsun-Kong Sham, Ruying Li, and Xueliang Sun  

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7.

**Title:** Interface design and coating materials applications of Li-S batteries

**Authors:** Xia Li and Xueliang Sun

The final version of this manuscript has been submitted in ACS applied materials and interfaces. All the authors contributed to designing, writing, and modifying the manuscript.
To the people I love
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<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>ALS</td>
<td>Advanced light Sources</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon black</td>
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<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
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<tr>
<td>CLS</td>
<td>Canadian light sources</td>
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<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
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<tr>
<td>C-S</td>
<td>Carbon-sulfur</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>C-ZIF</td>
<td>ZIF-8 derived carbon</td>
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<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>1, 3-dimethoxyethane</td>
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<tr>
<td>DOL</td>
<td>1, 3-dioxolane</td>
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<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
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<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>EG</td>
<td>Ethylene glycol</td>
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<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<td>EMC</td>
<td>Ethyl methyl carbonate</td>
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<td>EVs</td>
<td>Electric vehicles</td>
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<td>FA</td>
<td>Furfuryl alcohol</td>
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<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscope</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform-infrared</td>
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<tr>
<td>GO</td>
<td>Graphene oxide</td>
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<td>HEVs</td>
<td>Hybrid electric vehicles</td>
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<td>HEXPS</td>
<td>High energy X-ray photoelectron spectroscopy</td>
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<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
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<tr>
<td>HT</td>
<td>High temperature</td>
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<tr>
<td>LIBs</td>
<td>Li-ion batteries</td>
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<td>Li-S batteries</td>
<td>Lithium sulfur batteries</td>
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<tr>
<td>MLD</td>
<td>Molecular layer deposition</td>
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<tr>
<td>MOF</td>
<td>Metal organic framework</td>
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<td>MOF-C</td>
<td>Metal organic framework derived carbon</td>
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<tr>
<td>MPC</td>
<td>Micro/meso-porous carbon materials</td>
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<td>N-CNTs</td>
<td>Nitrogen doped carbon nanotubes</td>
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<tr>
<td>Abbreviation</td>
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<tr>
<td>NEXAFS</td>
<td>Near edge X-ray absorption fine structure</td>
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<td>N-MPC</td>
<td>Nitrogen doped micro/mesoporous carbon materials</td>
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<td>PANI</td>
<td>Polyaniline</td>
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<td>PEALD</td>
<td>Plasma enhanced atomic layer deposition</td>
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<tr>
<td>PEDOT: PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>RS</td>
<td>Raman spectroscopy</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>STEM-EDX</td>
<td>Energy dispersive X-ray spectroscopy-scanning transmission electron microscopy</td>
</tr>
<tr>
<td>SXRMB</td>
<td>Soft X-ray microcharacterization beamline</td>
</tr>
<tr>
<td>TEY</td>
<td>Total electron yield</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>TiN@C</td>
<td>Tin decorated porous carbon</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium isopropoxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>VLS-PGM</td>
<td>Variable line-spacing planar grating monochromator beamline</td>
</tr>
<tr>
<td>VMP-3</td>
<td>Versatile multichannel potentiostation 3/Z</td>
</tr>
<tr>
<td>XANE</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZIF</td>
<td>Zeolitic imidazolate framework</td>
</tr>
</tbody>
</table>
Chapter 1

1 Introduction

The exponential consumption of fossil fuels has driven a large exploratory effort in the search for sustainable renewable energy sources and energy storage systems. Batteries as a powerful successor have taken a dominant role for the application of large electrical devices [1, 2]. Since the introduction of Li-ion batteries (LIBs) by Sony in the early 1990s, these energy storage devices have been received extensive attention for the use in everyday-life portable devices, electrical grid, military, and electric vehicles (EVs) [3, 4]. Compared with other kinds of batteries, LIBs are competitive candidates owing to their high-energy density and long-cycle life [5, 6]. However, the energy output of current commercialized LIBs still cannot meet the requirements for the development of EVs and hybrid electric vehicles (HEVs) with long-driving range [5]. Owing to this inadequacy, the exploration of high-energy batteries is still critical for the development and application of Li-based batteries. Li-S and Li-air batteries are considered as next generation energy storage devices with superiorly high-theoretical capacity and energy density, and are well suitable for the use in EVs and HEVs [6-8]. In this introduction, configuration of Li-S batteries with detailed electrochemical mechanisms will be introduced. With the exception of the mechanism of Li-S batteries, recent reported literature in term of heteroatom doped carbon hosts and development of coating materials will also be summarized.

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1.1 Configuration of Li-sulfur and Li-ion batteries

Since the introduction in 1960s, Li-S batteries have always been considered as promising energy storage systems with ultrahigh theoretical energy density. However, the study of Li-S batteries stagnated until 2000 following the development of Li-ion batteries and the increasing demand for high energy output. Especially from 2009, Li-S batteries began to receive extensive attention after Linda Nazar first time developed secondary Li-S batteries with significantly improved cycle performance and cycle life [9]. Tremendous great effort has been carried out in the past decades to overcome the challenges of Li-S batteries.

![Figure 1.1 Configuration of Li-ion and Li-S batteries in terms of cathode and anode materials](image)

As shown in Figure 1.1, a typical Li-S battery is composed with three parts: cathode, anode, and electrolyte, which is closed to configuration of Li-ion batteries. Different from Li-ion batteries, for a typical Li-S battery, the cathode part is sulfur, and the anode part for most state-of-the-art Li-S batteries is lithium metal. For cathode part, sulfur has very low molar mass and it enables to generate multi-electrons per mole with Li metal. Based on these two characters, Li-S batteries composed with sulfur cathodes and lithium metal have
ultrahigh theoretical capacity and energy density. The electrochemical reaction mechanism of Li-S batteries is different from LIBs. Layered structured cathode and anode materials for Li-ion batteries are typically governed by intercalation/deintercalation processes [11-13]. Unlike LIBs, sulfur does not have layer or channel structure for Li-ions diffusion [6, 14]. A typical Li-S battery is governed by a solid-liquid dual-phase electrochemical reaction, which will be introduced in following section.

Table 1-1 Theoretical capacity, energy densities, and working voltage of cathode materials.

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>Working Voltage (V)</th>
<th>Theoretical Capacity (mAh g⁻¹)</th>
<th>Energy density (Wh kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>2.2</td>
<td>1675</td>
<td>2566</td>
</tr>
<tr>
<td>Li-O₂</td>
<td>3.0</td>
<td>3840</td>
<td>3505</td>
</tr>
<tr>
<td>Li-ion</td>
<td>3.0-5.0</td>
<td>100-270</td>
<td>400-700</td>
</tr>
</tbody>
</table>

The most appealing advantage of sulfur cathodes in Li-batteries is the ultra-high theoretical energy density (2600 Wh/kg). Compared to the lithium metal oxide cathode materials used in LIBs, elemental sulfur has a much lower molar weight while also being able to undergo multi-electron reactions with Li metal. These advantages allow sulfur cathode materials to have an ultrahigh theoretical specific capacity, nearly 10 times greater than current LIB cathode materials, as shown in Table 1-1 [15-18]. The working voltage of Li-S systems is mainly at 2.3-2.1 V and not as high as commercial cathodes of LIBs. However, this shortcoming is alleviated by the high specific capacity, resulting in an energy density over 5 times greater than commercialized metal oxide cathode materials. As shown in Figure 1.2, the practical packaged Li-S batteries enable to provide the specific energy of 400-600 Wh kg⁻¹, while the packaged Li-ion batteries is only less than 100 Wh kg⁻¹ with much higher price in unit. Moreover, the abundance, low cost, and environmental benignity of sulfur make it an attractive material for the use in next generation Li-based batteries [7, 19].
According to as mentioned advantages, Li-S batteries are considered as the most promising next generation batteries with high energy density.

**Figure 1.2** Specific energy and unit price of different batteries with potential drive range [14].

### 1.2 Challenges of Li-sulfur batteries

A typical Li-S battery is composed with sulfur cathode, Li metal as anode, and electrolyte to separate the two electrodes, as shown in **Figure 1.3**. The open circuit \((\Phi_{oc})\) of an assembled Li-S battery directly depends on the electrochemical potentials of lithium anode \((\mu_a, E^\Theta_a = -3.040 \text{ V})\) and sulfur cathode \((\mu_c, E^\Theta_c = -0.445 \text{ V})\), which is normally around 2.4-2.5 V [13]. A typical discharge process of sulfur cathodes is mainly in three segments: (I) Solid \(S_8\) molecules combine with Li-ions and open the ring to form long chain soluble polysulfides (solid phase to liquid phase), which the potential plateau is 2.3 V; (II) soluble long chain polysulfide is further reduced to solid \(Li_2S_2\) (liquid phase to solid phase), which the potential plateau is 2.1 V; (III) solid \(Li_2S_2\) is further reduced to final discharge product \(Li_2S\) (solid phase to solid phase) [20]. The electrochemical potential of sulfur cathode is increased with Li-ions insertion during discharge process and the terminal voltage \((\Phi)\) of batteries is normally lower than 1.5 V, as shown in **Figure 1.3b** [21]. The charge process is a reversed discharge process that \(Li_2S\) is oxidized to polysulfides and further formed sulfur and lithium metal, corresponding to 2.3 V and 2.4 V two potential plateaus, respectively. A typical cyclic voltammogram of Li-S battery is demonstrated in **Figure**
The cathodic and anodic peaks are well corresponded to discharge-charge potential plateaus. The III segment of discharge process does not show in CV profile due to the tiny differences in the potential between segment II and segment III [26-29].

Although high theoretical energy density of Li-S batteries, there are still many challenges accompanied with electrochemical reactions in this system [30-32]. For sulfur cathode, the first challenge is the natural insulation of sulfur (Electrical Conductivity $1 \times 10^{-15}$ S/m), resulting in diminished utilization of sulfur cathode in Li-S batteries [33-36]. The most popular strategy is accompanied with highly conductive material, most are carbon materials, to form sulfur based electrodes. However, the additive of carbon hosts will decrease the energy density of the whole battery. The dissolution of polysulfides is another serious issue pertinent to the sulfur cathode [37-41]. The dissolved long chain polysulfides will migrate to anode part and chemically react with lithium metal to form short chain polysulfides or solid Li$_2$S$_2$/Li$_2$S on the surface of lithium anode. Based on these side-reactions, the migration of dissolved polysulfides is called “shuttle effect”, and it results in serious corrosion of lithium metal and loss of sulfur active material. The third issue of sulfur cathode is the volume expansion of sulfur with Li-ion insertion [42]. The volume
expansion during battery cycling leads to cracked conductive network of sulfur electrode, resulting in decreased battery performance [43].

State-of-art Li-S batteries mostly employ lithium metal as an anode [44-50]. Although lithium metal anode results in high energy density, it suffers from a number of challenges when facing practical application [51, 52]. Firstly, lithium metal easily reacts with the surrounding electrolyte solvents, resulting in the formation of a solid electrolyte interlayer (SEI) on the surface of the Li metal [53, 54]. Part of this layer is irreversible during the electrochemical process and significantly hinders the insertion-desertion process of Li-ions, resulting in low coulombic efficiency and diminished cycle life for Li-S batteries [51, 55]. Additionally, the dissolved polysulfides found in Li-S batteries eventually migrate toward the lithium metal inevitably, resulting in the formation of insoluble Li2S/Li2S2 [56-59]. These side-reactions will cause serious corrosion of the Li metal, and also impede Li-ions transportation, resulting in requiring an excess of lithium metal and therefore, reduces the total energy density of the cell. Furthermore, lithium dendrite formation is also a crucial safety risk for Li-S batteries, which will cause short circuit or loss of energy density of batteries, as shown in Figure 1.4 [52, 55]. As reported in the literature, one advantage of Li-S batteries is that the dissolved polysulfides in ether based electrolyte will react with lithium metal surface, and retards the formation of lithium dendrite within Li-S batteries [13]. However, if the system utilizes other electrolyte systems (like carbonate electrolyte), or if very few polysulfides are dissolved into electrolyte, lithium dendrites may rapidly form, posing significant safety risks [60-62]. Thereby, protection for Li-metal is very essential for the application of Li-S batteries.
Electrolyte is one of crucial components in Li-S batteries [7, 8, 11]. Ether based electrolyte is the most popular one used in Li-S batteries, which enables to dissolve sulfur and improve the utilization for cells. However, it also brings “shuttle effect” as mentioned before [61, 64-66]. Besides, the boiling point and flash point of ether based solvents are very low [62]. For future application on electric vehicle, ether based electrolyte may raise safety hazards for Li-S batteries with elevated temperature operation. According to the physical properties of ether solvents, it will seriously limit the development of Li-S batteries in commercialization. Carbonate based electrolyte is not extensively applied in Li-S batteries due to the side-reaction between polysulfides and carbonate solvents, which needs to elaborately design of sulfur electrode to couple with carbonate electrolyte [61, 67-69]. Therefore, development of safe electrolyte for high energy Li-S batteries is very necessary in this field.

Based on these challenges, especially for the sulfur cathodes, researches focus on different strategies to break through the bottlenecks of Li-S batteries, such as developing carbon materials to improve the conductivity of sulfur composites; using coating materials to relief “shuttle effects”; and developing high sulfur areal loading cathode to enhance the energy density of batteries, etc. According to these reported literatures, the following segments will introduce and summarize two main nanomaterial approaches applied for sulfur
cathodes: (1) development of carbon hosts with heteroatom collaboration, and (2) coating materials applied in Li-S batteries.

1.3 The solutions of nanomaterials for sulfur cathodes

To achieve the practical use of Li-S batteries, use of carbon materials are seen as prevailing strategies to improve the conductivity of sulfur cathodes. Since Nazar et al. [9] reported highly ordered mesoporous carbon for Li-S batteries, various carbon materials have been employed in Li-S systems, including zero dimensional mesoporous particles [41, 70], one dimensional nanotubes and nanofibers [22, 25], two dimensional graphene [59, 71], and carbon paper [66, 72]. High conductivity, large pore volume, and desirable pore size of carbon materials are favorable to improve the conductivity of sulfur cathodes while maintain an elevated load of active sulfur material. Besides, it is widely accepted that the sorption effect and specific morphology of carbon nanomaterials effectively retain polysulfides in carbon matrix to relieve the deleterious “shuttle effect”.

Coating materials applied on sulfur cathodes are another effective strategy to keep sulfur from dissolution. During the past decades, many advanced nanomaterials and novel nanostructures have been reported as coating materials for sulfur cathodes [73-76]. According to differences of target materials, we will introduce coating applied on sulfur composites and on sulfur electrodes separately in this section. With the exception of coating material fabrication, novel nano-structures of coated sulfur cathodes along with their electrochemical performances will be summarized.

1.3.1 Development of novel carbon materials

Nitrogen-doped carbon materials have been extensively applied in energy storage devices including fuel cells [77, 78], Li-ion batteries [79, 80], Li-air batteries [81, 82], as well as many others fields [83, 84]. Their various applications in these fields are due to the metal free catalysis effect, high conductivity, distinct morphology, and specific surface properties. Two main synthetic routes are utilized for the production of nitrogen-doped carbon materials [85, 86]. One method employed for the in-situ inclusion of nitrogen into the carbon matrix is the use of a nitrogen containing precursor during pyrolysis [87-89]. This method is predominantly used in the fabrication of highly ordered structures such as
nitrogen-doped carbon nanotubes and nanofibers. Another strategy for the inclusion of nitrogen heteroatom is the use of a post-treatment method where nitrogen containing agents react with carbon materials to create various nitrogen doping types, including pyridinic, pyrrolic, and graphitic nitrogen [90-92]. Typically, this approach is generally conducted with ammonia gas under elevated temperature or with ammonium hydroxide in solvothermal process.

Meso- and microporous carbon materials (MPCs) are widely used in Li-S systems. Nitrogen-doped MPCs (N-MPCs) are predominately prepared by the post-treatment methods. Compared with pristine MPCs, N-MPCs have enhanced conductivity due to the electron configuration of N atoms. Furthermore, N-MPCs have the additional advantages of high surface area and large pore volume. These properties make N-MPCs ideal candidates as carbon hosts for sulfur cathodes. Research into the use of nitrogen-doped MPCs for Li-S systems was firstly reported in 2012 which proposed that N-MPCs may improve the conductivity of sulfur, resulting in high sulfur utilization during Li-S cycling process [93]. This study reported the use of nitrogen-doped mesoporous carbon (NC) as a host for sulfur cathodes. Compared with bare carbon-sulfur composite, NC/S composite showed a higher initial discharge capacity over 1400 mAh g\(^{-1}\), indicating enhanced sulfur utilization. Furthermore, NC/S is demonstrated lower sulfur cathodic potential, higher redox current density in the CV profile, and smaller surface charge transfer resistance in EIS test. These results are strong indications of improved electrochemical activity of sulfur due to the inclusion of nitrogen.
More recent research has concentrated on the exploration of the nitrogen effects and different reaction mechanisms in Li-S systems. Long et al. reported the use of nitrogen-enriched mesoporous carbon with tunable nitrogen content as host materials for sulfur cathodes [94]. The nitrogen-doped carbon/sulfur composites delivered a reversible discharge capacity of 758 mAh g$^{-1}$ at 0.2 C and 620 mAh g$^{-1}$ at 1 C over 100 cycles. The authors proposed that nitrogen doping facilitates the surface adsorption of polysulfide into mesoporous carbon, thus preventing polysulfide dissolution. Another research has further determined the catalytic effect of nitrogen doped carbon and demonstrated an economic strategy towards synthesizing sulfur/carbon composites via a bottom-up catalytic approach [95]. Nitrogen-enriched mesoporous carbon acts as a catalyst and oxidizes H$_2$S down to elemental sulfur, allowing sulfur directly formed onto the carbon framework to produce a C/S composite. The authors stated that nitrogen inclusion increases the surface interaction between polysulfides and carbon framework, resulting in the improved performance. The
composites exhibited a reversible capacity of 939 mAh g\(^{-1}\) after 100 cycles at 0.2 C and a rate capability of 527 mAh g\(^{-1}\) at 5 C after 70 cycles. These two reports clearly identify that nitrogen-doped carbon hosts can improve both capability and stability of Li-S batteries due to enhanced adsorption of polysulfides. However, there is as still a lack of understanding behind the exact mechanism that exists between doped nitrogen species and polysulfide species.

Except of “adsorption effect”, recent research has confirmed the presence of chemical interactions between N-doped carbon and sulfur-based species. Wang et al. [27] reported the interaction between nitrogen, oxygen and sulfur in sulfur cathodes. With the use of X-ray absorption near edge structure spectroscopy (Figure 1.5), the authors determined that nitrogen doping enable more sulfur accessible to oxygen functional groups on carbon, which is considered as a key role in sulfur immobilization. Recent research conducted by Sun et al. [96] also demonstrated the presence of chemical interactions between discharge products of lithium sulfides and N atoms from mesoporous carbon host by synchrotron-based X-ray photoelectron spectroscopy. The favorable interaction results in a uniform distribution of discharge products and drastically improves the electrochemical performance.

In Summary, the use of nitrogen-doped carbon for sulfur cathodes has undergone tremendous development, but further improvements in this field need to be established. Understanding of nitrogen doping effects in Li-S systems should be further studied. Two main effects of N-doped carbon have been proposed in literature. One is the improved conductivity of N-doped carbon, leading to high utilization of sulfur. The other is the immobility of polysulfides, resulting in stable cycle life. However, not enough work has been done to address the mechanisms governing these phenomena. Detailed research on the correlations between the nitrogen doping and sulfur cathode performance remains a challenge. Advanced characterization methods, such as synchrotron radiation analysis, can reveal the mechanisms behind the electrochemical performance. Synchrotron-based X-ray spectroscopy is a very powerful tool that can be used to understand the chemical structure of composites in Li-S systems. It has been confirmed by synchrotron radiation analysis: (1) the presence of interactions between graphene and sulfur via XAS spectroscopy [57]; (2)
the polysulfides transformation via operando XAS [97]; and (3) the dissolution effect of polysulfides via operando X-ray diffraction (soft X-ray) and transmission X-ray microscopy (hard X-ray) [98]. The research of synchrotron radiation on N-doped or other heteroatom doped carbon in Li-S batteries will shed light on the doping effect on electrochemical performance.

Furthermore, developing high quality and economic N-doped carbon materials is another challenge for applicable Li-S energy storage systems in future: (i) developing methods to synthesize mass-production of N-doped CNTs with low cost; (ii) identifying N doping types (pyridinic, pyrrolic, and graphitic nitrogen) on which is favorable for battery performance and developing approaches to control the percentages of desirable N doping type; (iii) understanding surface properties of N-doped carbon and finding ways to reduce the irreversible capacity loss of batteries resulting from doping effect [99]; (iv) improving other heteroatom-doped carbon materials for Li-S, Li-ion batteries, and other energy storage systems.

1.3.2 Interface design and coating materials for sulfur cathodes

Various researchers have devoted to overcome different challenges of Li-S batteries, such as development of carbon materials as sulfur hosts, optimization of electrolytes, coupling with high energy anode materials, et al [7, 19, 55, 100-103]. Among the currently published literature, understanding different interfaces of Li-S batteries and developing coating materials is one of the important directions in Li-S batteries, as shown in Figure 1.6b [6, 104-106]. This section summarizes the study of interface design and coating materials for Li-S batteries. The content covers structure design, synthesis approaches, electrochemical performance, reaction mechanisms, as well as future perspective of coating materials applied for Li-S batteries.
Figure 1.6 (a) Schematic figure of Li-S batteries and (b) different interlayers designed for Li-S batteries.

Dissolution of polysulfides and accompanied side-reaction “shuttle effect” is the severe challenge of sulfur cathodes [107, 108]. To overcome this challenge, designing an interlayer between the sulfur cathode and the electrolyte to retain sulfur and the polysulfides species within the cathode part is one effective solution [9, 109]. Coating materials are considered as a popular strategy toward designing this interlayer for sulfur cathodes to relief the “shuttle effect” in Li-S batteries. As shown in Figure 1.7, an ideal coating material for active materials in Li-ion batteries should possess following characteristics [110]: (1) an ultrathin and uniform coating, which can protect the active material from dissolution and still keep the properties of active material; (2) high Li-ion and electron conductivity; (3) good mechanical properties to protect active material with long cycle life [2, 4, 111]. Except of these properties, another important character of coating material for sulfur cathode is to accommodate the large volume expansion during cycling, which needs novel nanostructure and durable coating material for sulfur cathodes [112]. During the past decade, many advanced nanomaterials and novel nanostructures have been reported as a coating material for sulfur cathodes [73-76]. According to differences of target materials, we will introduce coating applied on sulfur composites and on sulfur electrodes separately in this section. With the exception of coating material fabrication, novel nano-structures of coated sulfur cathodes along with their electrochemical performances will be summarized.
1.3.2.1 Development of coating materials applied on sulfur based composites

I. Polymer based coating materials

Linda Nazar reported the use of highly-ordered carbon [9] as a host for sulfur. Following this numerous researchers have followed this approach using different kinds of carbon materials as sulfur hosts to improve the utilization of sulfur in cathodes [36, 61, 96]. To some extent, encapsulating sulfur in hosts help to relieve the “shuttle effect” in cycling. However, it still cannot completely halt the dissolution of polysulfides into the electrolyte. Based on this challenge, coating materials for sulfur cathodes seems necessary and a useful strategy toward addressing this issue. According to the low melting temperature (155 °C) and boiling temperature (~400 °C) of sulfur, the synthesis of coating material should be performed under mild conditions with relatively low temperature. Besides, the coating material still should meet a number of requirements such as good electrical and lithium ion conductivity, chemical stability, and light specific weight to maintain cathodic energy density. Therefore, carbon based materials such as conductive polymers and two-dimensional graphene are popular coatings applied for sulfur composites.

Polymers have been employed as coating materials for Li-ion batteries over decades. [113, 114]. The mild and facile synthesis process facilitates polymers growth on sulfur based composites, while high conductive polymers, such as polyaniline, polythiophene, and polypyrrole, et al., are favorable to improve the conductivity of sulfur cathodes [115, 116].
Early work of polymer coatings was conducted by a research team led by Dr. Wu who reported the use of polythiophene as a coating material for core/shell sulfur/polythiophene composites. [119]. During the synthetic process, Fe$^{3+}$ is used as a polymerizer to decorate the surface of sulfur particles and help in facilitating the thiophene monomer to polymerize on the surface of the sulfur particles, as shown in Figure 1.8a. Different ratios of the sulfur/polythiophene composites were characterized by elemental analysis. An optimized ratio for the composites was found to be 71.9 % sulfur and 18.1 % of polythiophene as determined by electrochemical results. The polythiophene coating layer acts as a conducting medium and a porous adsorbing agent for polysulfides, which bring improved cycle performance for Li-S batteries. The initial discharge capacity of the active material was found to be 1119.3 mAh g$^{-1}$, with a capacity of 830.2 mA h g$^{-1}$ after 80 cycles. Sulfur/polythiophene composites as a core-shell structure material improves the conductivity of the composite and also controls the morphology of the surface pore channels.

In the same year, Cui et al. reported the use of another conductive polymer, poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) as a coating material on sulfur-CMK composites, as shown in Figure 1.8b [118]. The battery performance and
corresponding characterization demonstrated that the conductive polymer PEDOT: PSS coating on the surface of mesoporous carbon/sulfur particles could be used to effectively trap polysulfides and minimize the dissolution of polysulfides and the loss of active mass in cathodes, which leads to a notable improvement in the performance of Li-S batteries. Later, Gao et al. used polyaniline as a coating material to cover sulfur-mesoporous carbon composites [117]. The research emphasized improved high-rate performance of sulfur cathode due to a synergistic effect between the high electrical conductivity from both the conductive carbon black in the matrix and the PANI polymer on the surface, as shown in Figure 1.8c. Following this pioneering work, many other researchers have aimed at using different conductive polymers as a coating material on various C-S composites or sulfur particles to demonstrate that a polymer coating material can both prevent the dissolution of polysulfides, and improve the conductivity of sulfur cathodes, as summarized in Table 1-2 [120-124].

II. Graphene based coating materials

Since the introduction of graphene in 2004, this carbon allotrope has been a popular material for use in a variety of energy storage systems [125-127]. The two dimensional structure, high conductivity, chemical and physical stability are very attractive properties of graphene as a coating materials [128, 129].
Dai et al. first reported the use of graphene-wrapped sulfur particles as a sulfur cathode material for Li-S batteries [130]. During the synthesis process, sulfur particles, coated with PEG containing surfactants, are used to facilitate the growth of graphene sheets on the sulfur particles, as shown in Figure 1.9a. The developed graphene-sulfur composite material is proposed to render sulfur particles electrically conductive, trap polysulfide intermediates, and sustain the stress and volume expansion of sulfur. The graphene-sulfur composites demonstrated high specific capacity with good cycling stability with specific capacities up to 600 mAh g$^{-1}$ over 100 cycles. In the same year, Nazar et al. reported graphene-enveloped sulfur composites for Li-S batteries, as shown in Figure 1.9b [21]. The research emphasized high coulombic efficiency of prepared graphene-sulfur composites with high sulfur weight loading (85 wt%). The author proposed that the graphene coating layer, with highly graphitic and slightly hydrophilic properties, enabled to formation of oxo-groups on the carbon surface, which facilitates absorption of polysulfide for sulfur cathode. These early work demonstrated graphene as a promising coating material for sulfur cathode which can not only improve the conductivity of the sulfur cathode, but also enable to capture dissolved polysulfides in some extent.
III. Challenges and obstacles of coating materials for sulfur composites

**Table 1-2** Summary of different carbon based coating applied for sulfur cathodes.

<table>
<thead>
<tr>
<th>Carbon based Coating</th>
<th>Sulfur load</th>
<th>Coating thickness</th>
<th>Cycle performance</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamline</td>
<td>43.7 wt%</td>
<td>10 nm</td>
<td>596 mAh g(^{-1})(0.1 C, 100 cycle)</td>
<td>[117]</td>
</tr>
<tr>
<td></td>
<td>70 wt%</td>
<td>20 nm</td>
<td>932 mAh g(^{-1})(100 mA g(^{-1}), 80 cycle)</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>80 wt%</td>
<td>N/A</td>
<td>765 mAh g(^{-1})(0.2 C, 200 cycle)</td>
<td>[131]</td>
</tr>
<tr>
<td>Polydopamine</td>
<td>81 wt%</td>
<td>N/A</td>
<td>955 mAh g(^{-1})(0.1 C, 200 cycle)</td>
<td>[132]</td>
</tr>
<tr>
<td></td>
<td>1.5 mg cm(^{-2}) &gt; 200 nm</td>
<td></td>
<td>900 mAh g(^{-1})(0.2 C, 150 cycle)</td>
<td>[133]</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>1.0 mg cm(^{-2})</td>
<td>10 nm</td>
<td>600 mAh g(^{-1})(0.5 C, 150 cycle)</td>
<td>[118]</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>71.9 wt%</td>
<td>20-30 nm</td>
<td>830 mAh g(^{-1})(100 mA g(^{-1}), 80 cycle)</td>
<td>[134]</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>60 wt%</td>
<td>N/A</td>
<td>600 mAh g(^{-1})(50 mA g(^{-1}), 20 cycle)</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>65 wt%</td>
<td>100 nm</td>
<td>600 mAh g(^{-1})(0.2 C, 50 cycle)</td>
<td>[136]</td>
</tr>
<tr>
<td></td>
<td>57.2 wt%</td>
<td>50 nm</td>
<td>880 mAh g(^{-1})(0.2 C, 100 cycle)</td>
<td>[137]</td>
</tr>
<tr>
<td>PETT-based polymer</td>
<td>1.5-2 mg cm(^{-2})</td>
<td>N/A</td>
<td>600 mAh g(^{-1})(0.5 C, 200 cycle)</td>
<td>[138]</td>
</tr>
<tr>
<td>Nafion polymer</td>
<td>70 wt%</td>
<td>N/A</td>
<td>~750 mAh g(^{-1})(0.1 C, 50 cycle)</td>
<td>[139]</td>
</tr>
<tr>
<td>Graphene-oxide</td>
<td>50.3 wt%</td>
<td>N/A</td>
<td>800 mAh g(^{-1})(1000 mA g(^{-1}), 1000 cycle)</td>
<td>[76]</td>
</tr>
<tr>
<td>Graphene wrapped sulfur-carbon fiber composites</td>
<td>66 wt%</td>
<td>N/A</td>
<td>694 mAh g(^{-1})(0.1 C, 50 cycles)</td>
<td>[75]</td>
</tr>
<tr>
<td>Graphene wrapped sulfur particle</td>
<td>70 wt%</td>
<td>N/A</td>
<td>600 mAh g(^{-1})(0.2 C, 100 cycle)</td>
<td>[130]</td>
</tr>
</tbody>
</table>

To our knowledge, in the past 5 years, a large amount of literature has reported the use of carbon based materials as a coating material for sulfur composites including conductive polymers, graphene materials, et al [32, 138, 140, 141]. These coating materials generally have mild synthetic procedures and are easily obtainable in most laboratory conditions with
minimal economic cost. For Li-S batteries, these in-situ formed coating materials mostly help to improve the conductivity of sulfur cathodes and relieve the “shuttle effect” for sulfur cathodes. However, it should be noted these coating materials still face a number of challenges: (I) the design of in-situ formed coating material does not address the large volume expansion of the sulfur cathode during the lithiation process. The coating material may become cracked or even detached from the sulfur composite, resulting in incomplete protection of the sulfur cathode and poor cycle life. (II) In-situ methods based within solution environments make controlling thickness and uniformity of the coating difficult. Based on aforementioned challenges, the next section will introduce some advanced nanostructure coating design for sulfur cathodes.

1.3.2.2 Design of hollow structured coating materials applied for sulfur composites

Volume expansion brings a number of challenges to the sulfur cathode during electrochemical cycling. Coating materials will eventually degrade due to the volume expansion from sulfur, making sustained long cycle life difficult [12, 55, 142]. Based on this challenge, it is critical and necessary to design novel nanostructured coating materials which enable to accommodate the volume expansion of sulfur cathode during lithiation process. To address this challenge, advanced research designed at fabricating different nanostructures to improve the function of the coating for sulfur cathodes are researched.

![Figure 1.10](image_url)

**Figure 1.10** Hollow nanostructure (a) yolk-shell structure and (b) O-ring structure of coating materials applied for sulfur composites [42, 43].
Cui with his research team firstly calculate the volume expansion of sulfur cathode and also raised the idea of maintaining “space” for sulfur cathodes with coating, as shown in Figure 1.10a [42]. They used TiO$_2$ as a coating material on sulfur particles, and then subsequently removed a portion of the sulfur to build enough internal void space between coating and the internal sulfur. Thereby, this yolk-shell structure can accommodate the volume expansion of sulfur cathode and minimize the dissolution of polysulfides into electrolyte. As a result, the yolk-shell structured sulfur-TiO$_2$ composites demonstrates stabilized, improved performance during cycling, demonstrating a capacity decay as small as 0.033% per cycle over 1,000 charge/discharge cycles. Following this idea, the yolk-shell structure applied for sulfur cathodes were also reported by other researchers, which employed different coating materials to pursue improved electrochemical performance of Li-S batteries [131, 133].

Although the yolk-shell coating structure results in improved protection for sulfur cathode, it is easily observed that the connection between the coating and the sulfur, separated by the void space, reduces the effective electronic path for sulfur cathode during electrochemical cycling. According to this issue, the new challenge is to design a coating structure that can provide space for sulfur while maintaining a stable connection. Cui et al. based on this design developed the O-ring structured PVP-sulfur composite, as shown in Figure 1.10b [43]. Different from the yolk-shell structure, the O-ring structure uses a conductive polymer coating with direct contact to sulfur. During the lithiation process, sulfur expands towards the center of the O-ring where enough space for volume expansion remains. The electrochemical performance showed improved cycling stability over 1,000 cycles with a capacity decay as low as $\sim 0.46$ mAh/g per cycle, demonstrating that the advanced nanostructure O-ring design as a coating material for sulfur cathodes is advantageous.

1.3.2.3 Atomic and molecular layer deposited coating applied on sulfur based electrodes

As denoted in the title, the coating materials introduced in this section are produced following electrode preparation, as shown in Figure 1.11a and 1.11b. Based on the “post-
formation” character, this coating structure aims to facilitate (I) preserving the conductive network of the electrode; (II) maintaining high sulfur loading. One strategy toward addressing this type of coating on the sulfur electrode is the use of atomic/molecular layer deposition (ALD/MLD). The following part will introduce details of applying ALD and MLD coating materials on the sulfur electrode as reported in literature.

**Figure 1.11** Comparison of coating material (a) applied on composites and (b) applied on electrodes. (c) Schematic figure of typical ALD coating process for Al$_2$O$_3$ using trimethylaluminium (TMA) and water [62, 143].

ALD/MLD is a novel ultrathin film gas-phase deposition technique [143-147]. It consists of utilizing self-limiting binary reactions, and demonstrates unparalleled advantages in producing uniform, conformal thin films, providing precise control over film thickness and chemical composition of the target material at an atomic and/or molecular scale, as shown in **Figure 1.11** [148-150]. The ultrathin and controllable film can aid in maintaining the high energy density of sulfur, while the uniformity of the coating facilitates the integrity of the protect sulfur cathode material [143, 149]. Furthermore, the low-temperature operation maintains the properties of sulfur electrodes at the most extent [111, 151, 152].
As shown in Figure 1.12a, Yushin et al. firstly reported the use of plasma-enhanced ALD (PEALD) to coat a sulfur cathode with Al\textsubscript{2}O\textsubscript{3} [153]. Interestingly, the coated sulfur-carbon fiber composite showed uniform morphology after cycling and retained a high sulfur loading within the electrode. Interestingly the lithium metal anode displayed a smooth surface morphology when used in conjunction with the PEALD coated sulfur cathode, demonstrating the protection from PEALD coating for sulfur cathode. The author also claimed that the ultrathin PEALD coating was able to maintain a high energy density for sulfur cathode. Following this experiment, other research groups have also reported the use of ALD Al\textsubscript{2}O\textsubscript{3} coating for various C-S electrodes, such as graphene-S composites, carbon black powder-sulfur composites, et al. [64, 154]. ALD Al\textsubscript{2}O\textsubscript{3} thin film has been found to not only be a simple and effective coating in preventing sulfur dissolution but has also been found to partially evolve into AlF\textsubscript{3} and LiAlO\textsubscript{2} during electrochemical cycling, resulting in a solid-state electrolyte that can improve the Li-ion transportation kinetics in the sulfur cathodes [64].
Sun et al. developed the use of an alucone coating using molecular layer deposition for use as a protective layer for the sulfur cathode [155]. The MLD alucone deposited thin film is similar to the ALD process [145, 156-158]. However, instead of using water as precursor to react with TMA the MLD process introduces an organic precursor during the oxidation pulse, in this case ethylene glycol is used to synthesize the alucone coating material. The MLD alucone coating material has a porous structure and improved mechanical properties compared to ALD Al$_2$O$_3$. This MLD alucone coating demonstrated different cycle performance compared to the ALD Al$_2$O$_3$ coated and the pristine C-S electrodes. The MLD alucone coated C-S electrode presented improved cycle stability and prolonged cycle life, and can be considered as a promising coating technology for sulfur cathodes and other energy storage systems [155].

Further, ALD and MLD ultra-thin film coating materials are notable to bring new electrochemical reactions, and also address many other challenges that face Li-S batteries. With the support of MLD alucone coating, Sun’s research team developed a safe and durable high-temperature Li-S battery, as shown in Figure 1.12b [62]. A major drawback for the popular Li-S electrolyte which are ether-based electrolyte, is their relatively low boiling and flash point, and thereby raises a plenty of safety issues for the use of Li-S batteries at temperatures > 50 °C [159]. On the other hand, carbonate-based electrolytes have been proven to be stable and have been widely accepted for use in high-temperature Li-ion battery application [160, 161]. However, most of sulfur cathodes are unable to complete reversible electrochemical process with Li anode due to the side-reaction between sulfur species and carbonate solvents. In an effort to address this issue Sun et al employed the use of an alucone MLD coating to provide a safe and versatile environment for sulfur cathode, and enable the operation of Li-S batteries in carbonate electrolyte. The alucone MLD coated C-S electrode demonstrate stable, and prolonged cycle life during operation at high temperatures. This novel method demonstrates how an alucone coating can effectively prevent side reactions from occurring between polysulfides and the carbonate solvent, thus enabling a solid-state Li-S electrochemical reaction to occur. It should be noted that although the research demonstrated improved performance of Li-S at high temperature, the cycle capacity and coulombic efficiency of alucone coated C-S electrode
at room temperature is still not ideal, and may related to inefficient use of Li anode and requires optimization of the carbonate-based electrolyte system [62].

In summary, the interlayer designed between the sulfur cathode and the electrolyte is proposed to prevent polysulfides dissolution and improve conductivity of sulfur. Plentiful coating materials for sulfur composites have been developed to protect sulfur from dissolution, providing new avenues to improve the performance for Li-S batteries. The latter novel hollow structure design of coating materials enable accommodation of the volume expansion for sulfur cathodes, which enhances the protection of sulfur with prolonged cycle life. This “space” idea is not limited for use in sulfur cathodes but also can be applied to other electrode materials, especially those that suffering from large volumetric expansion, such as silicon anode. However, it still should be noted that due to the space remaining and the integrity of the coating, this design inherently reduces the effective sulfur weight loading of the electrode, resulting in reduced specific energy density. Besides, controlling the thickness of the hollow structure design is difficult and will inevitably result in decreased energy density. From the author’s sight, pursuit of novel coating materials that are light-weight, ultrathin, and uniform with good mechanical properties are required in order to maintain long cycle life with high energy density of sulfur cathodes.

ALD/MLD technology is novel strategy to deposit ultrathin-film coating with precisely control over thickness and composition. The coating material, including metal-oxides, multi-element metal oxides, metal-organic hybrid composites, et al, can be tailored and designed depending on their use. Furthermore, ALD/MLD can be performed at relatively low temperatures and can uniformly coat high aspect ratio structures. These are properties which are beneficially for use on most electrode materials. This advanced approach enables the deposition of conformal thin film on different substrates and can be applied for both particle based composites and also formed electrodes. Although the conductivity of state-of-the-art ALD/MLD thin film still needs further development, it still should be considered as a promising coating technology for both Li-S batteries and other energy storage systems.
1.4 Thesis objectives

Li-S batteries are considered as most promising high energy storage systems which can be applied for EVs and HEVs. However, as mentioned before, sulfur cathodes still have a lot of challenges to address the high energy density, and it is believed that development of nanomaterials and novel nanostructure are one of crucial solutions to address these challenges.

In this context, the author devoted significant time to develop various nanomaterials as hosts for sulfur cathodes. Efforts were mainly on the synthesis of different carbon based nanomaterials, such as heteroatom doped carbon, metal-organic framework derived carbon, and ALD metal nitride decorated carbon. Further, dissolution of polysulfides is another serious issue of sulfur cathodes, the author focused on development of different coating materials for sulfur cathodes. The main research objectives are list below:

Part 1. Development of different carbon materials as host for sulfur cathodes.

(1) To develop different heteroatoms doped carbon as host materials for sulfur cathode, such as nitrogen-doped, oxygen-doped, and bare carbon materials. The heteroatoms effects on interaction with polysulfides species will be established.

(2) To develop ALD TiN decorated carbon as host materials for sulfur cathode. The influence of highly conductive TiN nanoparticle with polysulfides will be investigated from physical characterizations and electrochemical performance.

(3) To develop metal-organic-framework (MOF) derived carbon. Controlled porous structure of different MOF derived carbon (MOF-Cs) will be synthesized as hosts for sulfur cathodes, and detailed electrochemical performance and mechanisms of Li-S batteries in term of as-prepared MOF-Cs will be discussed.

Part 2. Development of different coating materials for sulfur cathodes.

(1) To develop atomic layer deposited (ALD) Al₂O₃ coating for sulfur cathodes. Different coating thickness of the coating and detailed electrochemical performance will be demonstrated.
(2) To develop molecular layer deposited (MLD) alucone coating for sulfur cathodes. Different MLD coating thickness, coating mechanisms, and comparison with ALD Al$_2$O$_3$ coating of sulfur cathodes will be discussed in detail.

(3) To develop safe and durable high temperature Li-S batteries with MLD alucone coating. Novel motivation and nanomaterial design will be proposed. Electrochemical performance of high temperature Li-S batteries and understanding with synchrotron based X-ray spectroscopy study will be investigated.

1.5 Thesis organizations

This thesis is consisted of nine chapters (two introductory chapters, six articles, and one conclusive chapter) and is organized according to the requirements on “Integrated-Article” form as outlined in the Thesis Regulation Guide by the School of Graduate and Postdoctoral Studies (SGPS) of the University of Western Ontario. It includes the following parts specifically.

Chapter 1 gives an introduction to lithium-sulfur batteries (Li-S). In this part, the electrochemical mechanism and challenges of Li-S batteries are introduced. Nanomaterial solution on the sulfur cathodes, including development of carbon nanomaterials and coating materials are highlighted. Further, the research objectives and the thesis structure are also stated.

Chapter 2 outlines the experimental synthetic approaches of as-prepared nanomaterials, and characterizations techniques applied to characterize the physical and electrochemical properties of materials and batteries.

Chapter 3 presents a study on the heteroatom doped carbon materials applied for sulfur cathodes. Controlled synthetic process with different heteroatoms doping is presented, and detailed mechanisms on the correlation between heteroatoms and the electrochemical reaction of sulfur cathodes are also studied.

Chapter 4 investigates another novel carbon material, which TiN decorated porous carbon material applied for sulfur cathodes. As-prepared TiN decorated carbon via atomic layer
deposition provides improved conductivity for sulfur cathode which facilitated the high rate performance for Li-S batteries. In addition, the interaction between TiN and polysulfides helps to relieve side reactions of sulfur cathode, which brings significantly improved electrochemical performance for Li-S batteries.

**Chapter 5** reports a novel MOF derived carbon material (MOF-C) for sulfur cathodes. Effects of different porous structure of MOF-C on electrochemical reactions of Li-S batteries are investigated. The research work also presents detailed study on the control of MOF-C nanomaterials in terms of morphology, surface area, and porous structure via a novel gas treatment approach.

**Chapter 6** represents atomic layer deposited Al₂O₃ as coating materials for sulfur cathode. ALD Al₂O₃ coating enables to effectively prevent the dissolution of polysulfides and stabilizes the cycled capacity of sulfur cathodes. Besides, ALD Al₂O₃ coating can be transferred to AlF₃ and LiAlO₂ during cycling, which is benefit to Li-ion transportation for sulfur cathodes. The study also presents the thickness effects of coating layer on the electrochemical performance of Li-S batteries at last.

**Chapter 7** fulfills a novel coating material, named molecular layer deposited alucone coating material applied for sulfur electrode. The MLD alucone coated electrode demonstrates improved cycle performance and prolonged cycle life. Detailed mechanisms of alucone coating on the electrochemical reaction of Li-S batteries are studied. Besides, comparison of ALD Al₂O₃ coating and MLD alucone coating is also presented in this part.

**Chapter 8** explores how to address safe and durable high temperature Li-S batteries with MLD alucone coating. The study found that carbonate based electrolyte gives a safe and stable environment for batteries at high temperature, and MLD alucone coating helped sulfur cathode successfully operating in carbonate electrolyte without side-reactions. Detailed electrochemical processes with deep understanding on the mechanisms via synchrotron based X-ray beamline are investigated in this chapter.
Chapter 9 summarizes the results and contributions of the thesis work. Furthermore, the author states some personal opinions, perspective, and suggestions for future Li-S batteries and energy storage development.
References


3257.


Chapter 2

2  Experimental Apparatus and Characterizations Techniques

In this chapter, the synthetic approaches of nanomaterials, as well as physical and electrochemical characterization techniques are states here.

*Part of version of this chapter has been published in J. Mater. Chem. A, 2014, 2, 12866; J. Power Sources 2016, 302, 174*
2.1 Experimental apparatus

2.1.1 Synthesis of porous carbon materials

Commercial carbon black N330 was chosen as a starting material. Nitrogen inclusion was carried out by pyrolyzing 500 mg of carbon black powder under NH$_3$ at 1050 °C for 3-5 minutes, yielding a highly porous structure. Previous reports have indicated that NH$_3$ reacts with carbon black with the following reaction mechanism: [1]

\[ C + NH_3 \rightarrow HCN + H_2 \]

\[ C + H_2 \rightarrow CH_4 \]

Oxygen species were introduced into N330 in a similar procedure with the use of CO$_2$ gas. The reaction occurs in the following manner: [2]

\[ C + CO_2 \rightarrow CO \]

The oxygenated sample was then further pyrolyzed under H$_2$ at 950 °C to remove oxygen bearing functional groups. Herein, carbon blacks treated under NH$_3$, CO$_2$, and CO$_2$/H$_2$ are named as N-N330, O-N330, and RO-N330, respectively.

2.1.2 Synthesis of metal organic frameworks derived carbon materials

The synthesis of ZIF-8 derived carbon follows the approach reported by Xu’s group [3]. Typically, commercial zeolite-type metal-organic framework ZIF-8 (Basolite Z1200, Sigma-Aldrich) and furfuryl alcohol (FA, Sigma-Aldrich) were used as the starting materials. FA was firstly introduced into ZIF-8 to obtain FA/ZIF-8 composites under an evacuated environment. The FA/ZIF-8 composites were then transferred into a furnace under Ar atmosphere and heated in a program at 80 °C for 24 h, then at 150 °C for 6 h, and finally at 1000 °C for 8 h to obtain ZIF-8 derived carbon (C-ZIF). The obtained C-ZIF was then in-situ treated under ammonia atmosphere at 1050 °C for 3, 5, and 7 min to form different porous structures, as shown in Figure 2.1. The obtained samples are referred as N3-C, N5-C, and N7-C.
2.1.3 Atomic layer deposition and molecular layer deposition systems

Atomic layer deposition was conducted in a Savannah 100 ALD system (Cambridge Nanotech, USA), as shown in Figure 2.2. ALD Al₂O₃ coating was grown on the C/S electrode at 100 °C by using trimethylaluminium and H₂O as precursors. To obtain Al₂O₃ coatings with different thicknesses, 2-, 5-, 10-, and 20-cycle Al₂O₃ by ALD were conducted directly on sulfur-carbon electrodes at 100 °C using TMA and H₂O as precursors (see details in ESI). On the basis of ALD mechanism, the thickness of coating layer should be linearly increased with stepwise ALD reactions. The thicknesses of 2-cycle and 20-cycle ALD coating are about 0.2 and 3 nm theoretically.
Molecular layer deposition of alucone was conducted in a Gemstar-8 ALD system (Arradiance, USA), as shown in Figure 2.3. Alucone was directly deposited on the C-S electrode at 100 °C by alternatively introducing trimethylaluminium (TMA) and ethylene Glycol (EG). As studied from previous research, the growth rate of alucone thin film is < 0.3 nm/MLD cycle, and the sulfur loading of the C-S electrode dropped by 5 wt% after alucone coating.

2.2 Characterizations techniques

The physical and chemical properties of nanomaterials, such as morphology, nanostructure, components, chemical bonding, surface area, and porous structure, et al. have been determined via varies of analytical techniques, such as scanning electron microscope (SEM), Raman spectroscopy (RS), Fourier Transform Infrared Spectroscopy (FT-IR), Energy Dispersive Spectroscopy (EDS), X-ray diffraction (XRD), etc. To investigate the electrochemical properties of as-prepared nanomaterials, discharge-charge cycle performance with different current densities, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were conducted with assembled half-cells.
2.2.1 Physical characterizations

The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectroscopy (EDS), as shown in **Figure 2.4**. Raman scattering (RS) spectra was obtained using a HORIBA Scientific LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser, as shown in **Figure 2.5**. Fourier transform-infrared (FTIR) measurements were determined by KBr method with a Nicolet 6700 FT-IR recorded in the transmittance mode over range of 400-4000 cm\(^{-1}\) spectra by averaging 40 scans with a resolution of 8 cm\(^{-1}\). Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min on the SDT Q600 (TA Instruments).

**Figure 2.4** A photo of Hitachi S-4800 high resolution scanning electron microscope.
Surface area and porous structure were determined by N\textsubscript{2} adsorption/desorption isotherms were conducted via Folio Micromeritics TriStar II 3020 Surface Area and Pore Size Analyzer, as shown in Figure 2.6. The surface area of the nanomaterials was used by the Brunauer, Emmett, and Teller (BET) model. Porous structure was determined by the Barrett, Joyner, and Halenda (BJH) model. X-ray diffraction spectra were obtained using a Bruker D8 Advance (Cu−K\textalpha source, 40 kV, 40 mA).
2.2.2 Electrochemical characterizations

CR-2032 type coin cells were assembled in an argon-filled glove box. The coin-type cells consisted of Li foil as the anode, polypropylene membrane (Celgard 2400) as separator, and the prepared C-S electrode as the cathode. Two electrolyte systems were selected in this research: (1) carbonate-based electrolyte composed of 1 M LiPF$_6$ solution in ethylene carbonate: diethyl carbonate: ethyl methyl carbonate (EC:DEC:EMC) with a volume ratio of 1:1:1, and (2) ether-based electrolyte composed of 1 M LiTFSI salt in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio.

![Figure 2.7 An appearance of VMP3 Potentiostat/Galvanostat/EIS system.](image)
Cyclic voltammograms (CVs) were collected on a versatile multichannel potentiostation 3/Z (VMP3), as shown in Figure 2.7 under a scanning rate of 0.1 mV s\(^{-1}\) between 1.0 V - 3.0 V (vs. Li/Li\(^+\)). Electrochemical impedance spectroscopy (EIS) was also performed on the versatile multichannel potentiostat 3/Z (VMP3) by applying an AC voltage of 5 mV amplitude in the 100 kHz to 100 mHz frequency range. All of batteries were tested by holding 6 hours after assembling. Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V - 3.0 V (vs. Li/Li\(^+\)) at room temperature using an Arbin BT-2000 Battery Test equipment, as shown in Figure 2.8.

References


Chapter 3

3 Carbon blacks as cathode hosts applied in lithium sulfur batteries: Effect of heteroatom-doping

Low conductivity is one crucial challenge of sulfur cathodes and therefore high conductive carbon materials are employed as host materials accompanied with sulfur to improve the conductivity of sulfur. As report, heteroatoms doping bring new properties for carbon materials, such as nitrogen doping, which has been demonstrated improved electron conductivity for N-doped carbon.

On the other hand, deposition of insulated discharge products, Li$_2$S and Li$_2$S$_2$, also directly affects the electrochemical performance of Li-S batteries. The uniform deposition of discharge products facilitates the reversible electrochemical process, which improved the cycle life of Li-S batteries. Heteroatoms doped carbon materials may bring active sites for discharge product deposition, and the interaction between sulfur species and heteroatoms in carbon matrix may also prevent polysulfides dissolution.

In this chapter, different heteroatoms doped carbon materials are prepared via gas-phase treatment and the as-prepared samples are employed as carbon hosts for sulfur cathodes. With controllable porous structure (surface area, pore size, pore volume, etc.), the research investigates the effect of heteroatoms on electrochemical performance of sulfur cathodes. It is demonstrated nitrogen doped carbon provides improved conductivity and also facilitates the discharge product uniformly deposition in carbon matrix. Further, it is found that sulfur is partially oxidized by oxygen-functional carbon which deteriorates the performance of sulfur cathodes.

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3.1 Introduction

Recently, Li-sulfur batteries have been considered as powerful energy storage systems that can be utilized in the electric vehicles [1]. Associated with its light atomic weight and potential multiple-electron reaction, sulfur as cathode material endows an overwhelmingly high theoretical capacity and energy density [2-4]. Furthermore, sulfur is an abundant, and environmental benign element with low production costs, making Li-sulfur batteries a competitive candidate for next generation battery systems. However, two main issues impede the practical application of Li-sulfur batteries [2-4]. The first is the inherent insulating nature of sulfur and lithium sulfide, resulting in limited performance of Li-sulfur batteries [1-3, 5]. Secondly, dissolved polysulfides migrate between the cathode and anode as called the “shuttle effect” and participate in unexpected side reactions, resulting in lithium metal corrosion and drastic loss of sulfur active material [5-8].

To address these issues, carbon nanomaterials have been applied as sulfur cathodes due to their high conductivity, high pore volume and fitted pore size, such as mesoporous carbon black, one dimensional carbon nanofibers and nanotubes, and two dimensional graphene [9-11]. Recently, carbon materials used for sulfur cathodes have also been extended by introducing heteroatoms into the carbon matrix [12-17]. Wang et al [14] revealed that the introduction of nitrogen enhanced the chemical adsorption between sulfur and oxygen species of carbon. Archer et al [13] stated that the Li-N interaction is responsible for uniform Li$_2$S deposition on nitrogen-enriched polymers, leading to improved electrochemical performance of Li$_2$S based cathode materials. These researches demonstrated that carbon-heteroatom bonds alter the electrochemical performance of sulfur cathodes. However, the effects of other heteroatoms, such as oxygen, embedded into carbon matrix have not been extensively explored.

In this paper, various treatments are employed on commercial carbon black to introduce nitrogen and oxygen heteroatoms. The treated carbon blacks have comparable physical properties (surface area, pore size, and pore volume), and serve as a good system towards isolating the effect of heteroatoms on the performance of sulfur cathodes. In-depth
discussion by synchrotron-based XPS was carried out to reveal electrochemical mechanisms.

3.2 Experimental

3.2.1 Preparation of carbon blacks

Commercial carbon black N330 was chosen as a starting material. Nitrogen inclusion was carried out by pyrolyzing 500 mg of carbon black powder under NH$_3$ at 1050 °C for 3-5 minutes, yielding a highly porous structure. Previous reports have indicated that NH$_3$ reacts with carbon black with the following reaction mechanism: [18]

\[
C + NH_3 \rightarrow HCN + H_2
\]

\[
C + H_2 \rightarrow CH_4
\]

Oxygen species were introduced into N330 in a similar procedure with the use of CO$_2$ gas. The reaction occurs in the following manner: [19]

\[
C + CO_2 \rightarrow CO
\]

The oxygenated sample was then further pyrolyzed under H$_2$ at 950 °C to remove oxygen bearing functional groups. Herein, carbon blacks treated under NH$_3$, CO$_2$, and CO$_2$/H$_2$ are named as N-N330, O-N330, and RO-N330, respectively.

3.2.2 Preparation of sulfur-carbon black composite

As-prepared carbon blacks were mixed with pristine sulfur and dried at 80 °C for 12 h to remove moisture. The sulfur-carbon black mixture was transferred to a sealed steel reactor and heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained sulfur-carbon black composites had a sulfur loading of 60 ± 2 wt% and were confirmed with thermogravimetric analysis (TGA). Sulfur carbon black composites are in term of S/N-N330, S/O-N330, and S/RO-N330, separately.
3.2.3 Physical characterization

Morphological observations were characterized using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operating at 5 KeV. TGA was carried out on a TA SDT Q600 in N$_2$ atmosphere from room temperature to 700 °C at a rate of 10 °C/min. N$_2$ adsorption/desorption isotherms of carbon blacks were collected by Folio Micromeritics TriStar II Surface Area and Pore Size Analyzer. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra Al α unit. Raman scattering (RS) spectra was obtained using a HORIBA Scientific LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser. Fourier transform infrared (FTIR) measurements were determined by KBr method with a Nicolet 6700 FT-IR recorded in the transmittance mode over range of 400-4000 cm$^{-1}$ by averaging 40 scans with a resolution of 8 cm$^{-1}$. Synchrotron-based XPS was conducted on the variable line spacing planegrating monochromator (VLS PGM) beamline at the Canadian Light Source (CLS), located at the University of Saskatchewan in Saskatoon [20].

3.2.4 Electrochemical characterization

CR-2032 type coin cells were assembled in an argon filled glove box. Assembled batteries were made using Li metal as an anode, a polypropylene separator, and as-prepared electrode as cathode. 1M LiTSFI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) in a 1:1 volume ratio was used as the electrolyte. The electrodes were prepared by slurry casting on aluminum foil as a current collector. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluorides (PVDF) was 7:2:1. The as-prepared electrodes were dried at 80 °C over 12 h under vacuum. Cyclic voltammetry (CV) was collected on a versatile multichannel potentiostation 3/Z (VMP3) under a scanning rate of 0.1 mV/s between 1.0 V-3.0 V (vs. Li/Li$^+$). Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V-3.0 V (vs. Li/Li$^+$) at room temperature using an Arbin BT-2000 Battery Tester.
3.3 Results and discussion

Previous research has indicated that the physical surface properties (morphology, surface area, pore volume, and pore size) of carbon materials have a significant influence on the performance of sulfur cathodes [2-4]. In order to isolate the role of heteroatoms in Li-S battery systems, carbon materials with similar physical surface properties but different heteroatoms needs to be used. Figure 3.1 shows FE-SEM images of as-prepared carbon blacks. Morphologies across all three samples indicate that nanoparticles are agglomerated and are within 30-50 nm. As shown in Table 3-1, as-prepared carbon blacks have comparable physical surface properties with surface areas between 1200-1300 m² g⁻¹; pore volumes in the range of 1.15-1.25 cm³ g⁻¹; and a mean pore size between 3-4 nm. The mechanism of porous structure formation has been well previously described by Jaouen et al [18, 19, 21]. Pristine carbon black N330 is a spherical carbon particle without pores, consisting of disordered carbon and graphitic carbon (Figure 3.1d). During the heteroatom doping process, NH₃ or CO₂ is proposed to react with both graphitic and disordered carbon but in different reaction rate, resulting in the formation of porous structure for carbon blacks. With the carbon black consumed, micropores increase in size, producing a mesoporous structure [18, 19]. Pore formation is conducted in a similar manner under different atmospheric conditions (CO₂ or NH₃), thereby the three carbon blacks are comparable in physical surface properties.
Figure 3.1 FE-SEM images of carbon blacks (a) N-N330 (b) O-N330, (c) RO-N330 and schematic of (d) porous structure formation of as-prepared carbon blacks.

Table 3-1 Physical surface properties of carbon blacks

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Specific surface (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Mean Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-N330</td>
<td>1208.98</td>
<td>1.228</td>
<td>4.3</td>
</tr>
<tr>
<td>O-N330</td>
<td>1325.45</td>
<td>1.120</td>
<td>3.3</td>
</tr>
<tr>
<td>RO-N330</td>
<td>1345.66</td>
<td>1.166</td>
<td>3.5</td>
</tr>
</tbody>
</table>

XPS survey spectrum of N-N330 confirms the introduction of nitrogen (N doped or N functional groups) into carbon black with a concentration of 1.5 at%, as shown in Figure S3.1. FTIR spectra (Figure S3.2) of O-N330 displays C-O related vibrations appearing at 1470 cm⁻¹ and 720 cm⁻¹, demonstrating the successful introduction of oxygen-bearing functional groups [22, 23]. Based on the above results, we have successfully created a system where the role of heteroatoms in Li-S batteries can be isolated and studied.
Figure 3.2 Cycle performance at (a) 0.1 C and (b) various current densities of sulfur-carbon black cathodes

Cycling performance of sulfur cathodes at 0.1 C (160 mAh g\(^{-1}\)) are outlined in Figure 3.2a. The three samples present similar tendencies in cycling stability, accounting for the similar physical properties of carbon blacks. Interestingly, S/N-N330 delivers impressive discharge capacities with an initial discharge capacity of about 1490 mAh g\(^{-1}\), indicating very high sulfur utilization (87 %). After 40 cycles, the discharge capacity of S/N-N330 maintains about 1020 mAh g\(^{-1}\). Moreover, S/N-N330 exhibits an elevated coulombic efficiency of 93 %, confirming a high reversibility Li-S redox reaction. However, the S/RO-N330 and S/O-N330 show relatively lower capacities and coulombic efficiencies. Especially, S/O-N330 only presents a capacity of 550 mAh g\(^{-1}\) after the 40th discharge cycle. The rate performance is also one of great concern on rechargeable batteries. As shown in Figure 3.2b, S/N-N330 is demonstrated significantly better rate performance compared to S/O-N330 and S/RO-N330, with a capacity of over 700 mAh g\(^{-1}\) under 6.4 A g\(^{-1}\) after 70 cycles, indicating excellent tolerance to drastic current density alterations during battery cycling.
Detailed analysis of electrochemical reactions was conducted by cyclic voltammetry. **Figure 3.3a** shows the normalized CV profiles at a scanning rate of 0.1 mV s\(^{-1}\). Two cathodic peaks at 2.3 V and 2.1 V, and one anodic peak at 2.5 V are shown in the first sweeping cycle, correlating with discharge-charge potential plateaus displayed in **Figure 3.3b**. The two cathodic peaks are associated with the two-step discharging process, consistent with prevailing Li-S mechanism [24-27]. During the cathodic process, sulfur firstly reduced into S\(_8\), corresponding to the cathodic peak at 2.3 V; then stepwise reduced into low-order polysulfides (S\(_{2}\), S\(_{2}\)), corresponding to the peak at 2.1 V [28-30]. Interestingly, N-N330 performs much lower anodic peak intensity than that of RO-N330 while the two cathodic peak intensities are comparable, implying shuttle effect relief by N-N330 host. On the other hand, the normalized peak area of S/O-N330 is much smaller than that of the other two samples. This may be due to the limited electrochemical activity and reduced cycling performance seen during the cycling performance. The aforementioned electrochemical performance results highlight the improved performance of N-N330 over O-N330 and RO-N330 samples, with O-N330 demonstrating dramatically reduced performance. The following discussion will elucidate the reason of heteroatom effects on the significant difference of electrochemical performances.
Figure 3.4 Synchrotron-based S 2s XPS spectra of sulfur-carbon black composites.

Figure 3.4 shows the synchrotron-based XPS spectra for sulfur 2s core level of sulfur-carbon black composites. Interestingly, S/O-N330 shows an additional peak at higher binding energy, indicating that a part of sulfur is oxidized to a higher valence state. This information correlates will with FTIR spectra obtained for S/O-N330 (Figure S3.3), where the presence of S-O bonds is clearly visible. Along with the reduced cycling performance of S/O-N330, these results suggest that an unexpected reaction occurs between sulfur and surface oxygen species to form S-O functional groups. These unwanted side reactions may arise as a result of three issues: (1) loss of active sulfur material during cycling; (2) deterioration of host conductive carbon material; and (3) elevated irreversible product formation during cell operation [31-33].
The mechanism of discharge product formation for Li-sulfur batteries is based on the electrical conductivity of the electrode, sorption effects of the carbon host, and reversibility of Li-sulfur reactions [34, 35]. As shown in the SEM images of Figure 3.5, S/N-N330 electrodes maintain their initial morphology, while S/RO-N330 and S/O-N330 electrodes display sphere-like and even aggregating slab-like discharge products deposited on the surface (as outlined in red). This provides strong evidence that the discharge products of S/N-N330 are more uniformly distributed across the substrate surface as a result of nitrogen inclusion.
Figure 3.6 Raman spectra of as-prepared carbon blacks, inserted form is the value of ID/IG of carbon blacks.

Raman spectra of carbon blacks were conducted to determine the graphitic order of carbon following NH$_3$, CO$_2$ and CO$_2$/H$_2$ treatment (Figure 3.6). D (1350 cm$^{-1}$) and G bands (1590 cm$^{-1}$) are associated to disordered and graphitic carbon phase, respectively [36, 37]. The value of peak intensity ratio of D and G band are given in the table inserted in Figure 3.6. N-N330 carbon black exhibits a higher Id/Ig ratio than O-N330 and RO-N330, indicating a greater inclusion of defect sites on the surface. It has been confirmed in our previous work that enriched defect sites are favorable to uniform discharge product deposition in Li-air batteries [38]. In our case, the discharge product Li$_2$S or Li$_2$S$_2$ may be also attracted by nitrogen introduced defect sites, leading to uniform discharge product formation.
Figure 3.7 Synchrotron-based Li 1s XPS spectra of sulfur electrodes after cycling.

Synchrotron based Li 1s XPS spectra of electrodes after 30 discharge-charge cycles supports this explanation, as shown in Figure 3.7. Peaks for RO-N330 appear at 55.5 eV which can be attributed to Li 1s electrons in Li$_2$S [39, 40]. Interestingly, peaks for N-N330 showed a slightly shift to lower binding energy, corresponding to interactions occurring between Li and nitrogen donated electrons [41]. The interaction between Li and nitrogen is favorable to the uniform dispersed discharge product. It is not very clear why peak of O-N330 shows tiny shift to higher binding energy but it may derive from the formation of LiSO$_x$ or Li$_2$O$_x$ [39, 42].
Based on the analysis and conclusions drawn above, a schematic diagram of the process for the three sulfur-carbon black cathode systems is outlined in Figure 3.8. The enriched defect sites and interaction between lithium and nitrogen of N-N330 result in uniform distribution of small sized discharge products, thereby improving sulfur utilization and reversibility of Li-S redox reactions, ultimately yielding improved electrochemical performance. RO-N330 has fewer defects sites, resulting in the formation of larger sized discharge products aggregating on the surface. The O-N330 carbon black undergoes unexpected side reactions with sulfur, leading to a reduced conductivity of electrode and a serious growth aggregation of slab-like discharge products, resulting in significantly reduced cycling performance.

3.4 Conclusions

In order to reveal the influence of heteroatom effects on sulfur cathodes, we developed a series of carbon materials with similar physical structure. Commercial N330 carbon black was treated with NH$_3$, CO$_2$, and CO$_2$/H$_2$ to prepare nitrogen-introduced, oxygen-
introduced, and bare porous carbon blacks, respectively. The three sulfur-carbon black composites with different heteroatoms showed varying electrochemical performances. It was found that the enriched defect sites and favorable interaction between N atoms and discharge products result in a uniform distribution of discharge product in carbon matrix and thereby give improved electrochemical performance. The O-N330 carbon black underwent unwanted side reactions with sulfur, leading to low sulfur utilization and large slab-like discharge product formation on the electrode. Our work demonstrated that an important correlation exists between carbon-heteroatom bonds and battery performance, and opens a novel direction towards the optimization of carbon host materials used for Li-sulfur batteries.

Acknowledgements
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References


Supporting Information

Figure S3. 1 XPS survey spectrum of N-N330.

Figure S3. 2 FTIR spectra of as-prepared carbon blacks.
Figure S3. 3 FTIR spectra of O-N330, S/O-N330, and pristine sulfur.

Figure S3. 4 XRD patterns of as-as prepared carbon blacks.
Table S3-1 Surface information of carbon blacks treated by NH$_3$ with different mass loss

<table>
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<tr>
<th>Reaction time (min)</th>
<th>Mass loss (wt%)</th>
<th>Specific Surface area (m$^2$/g)</th>
<th>Specific surface area for mesopores (m$^2$/g)</th>
</tr>
</thead>
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<tr>
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</tr>
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</tr>
<tr>
<td>8</td>
<td>85</td>
<td>1358.27</td>
<td>1181.90</td>
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</table>
Chapter 4

Titanium nitride catalyst supported sulfur cathodes via atomic layer deposition with high rate performance for Li-S batteries

As report, nitrogen-doped carbon facilitates the electrochemical performance of sulfur cathode due to the high conductivity and active sites. Recently, titanium nitride (TiN) has been concerned as a novel conductive metal nitride nanomaterials in energy storage fields. The conductive TiN is considered as an effective catalyst to active solar cell reactions in dye sensitized solar cells. Besides, titanium based metal oxides has been found strong interaction with polysulfide species, which significantly prevents “shuttle effect” side-reactions. Based on aforementioned research, TiN is very suitable as catalyst for sulfur cathodes to improve the electrochemical performance of Li-S batteries.

In this chapter, TiN decorated porous carbon (TiN@C) was synthesized via atomic layer deposition (ALD) and gas-phase annealing treatment. The as-prepared sample is demonstrated the uniformly distribution of TiN on porous carbon with less 2 nm nanoparticle size. From electrochemical characterization, the as-prepared TiN@C as carbon host demonstrated significantly improved high-rate performance and stabilized cycle life of sulfur cathodes. Detailed mechanism study was present to investigate the mechanism of TiN in sulfur cathode.
4.1 Introduction

Li-S batteries have been receiving a great deal of attention recently due to their ultrahigh theoretical energy density, and are considered as a promising candidate as an energy storage system for long range electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1-3]. However, there are many issues that plague the sulfur cathode and hinder this technology’s commercialization [4-6]. Firstly, the insulating nature of sulfur results in low utilization of active material during electrochemical cycling, leading to poor cyclic capacity. Further, the intermediate products formed during cycling, lithium polysulfides, are highly soluble in the electrolyte and partake in corrosive reactions at both the anode and cathode, often coined as the “shuttle effect” [4-6]. The long chain polysulfides migrate through the separator and chemically react with the Li metal anode. Reduced short chain polysulfides reverse back to the cathode where they are chemically oxidized by long-chain polysulfides. The “shuttle effect” gives rise severe Li metal corrosion and loss of active sulfur material, leading to rapidly diminishing electrochemical performance [7-10].

Employing conductive host materials accompanied with sulfur is one solution to overcome the challenges mentioned above [1, 3]. Carbon materials are the material of choice as a sulfur hosts for sulfur cathodes due to their high conductivity, sufficient surface area, and sorption effect in trapping polysulfides [4, 6, 8, 11, 12]. To further improve the host material, recent research has focused on introducing catalytic effect during the Li-S electrochemical reaction to elevate rate performance and cyclic stability. Nitrogen doped carbon materials and metal oxide nanoparticles are reported as catalysts to provide more active sites for discharge product deposition and dissolved polysulfides trapping [13, 14]. As demonstrated in literature, an ideal catalyst should facilitate the Li-S redox reaction and prevent side-reactions for occurring. Furthermore, the catalyst should be designed to ensure maximum contact with the active species for the duration of the cycle life. Therefore, it is crucial to design a conductive catalysts with ultra-uniform distribution on carbon host for sulfur cathode.
For the first time, conductive titanium nitride supported carbon (TiN@carbon) via atomic layer deposition (ALD) is used as a host material for sulfur cathodes. TiN is well known as a catalysts for electrochemical reactions, and has been applied for use in both dye sensitized solar cell and Li-ion batteries [15-18]. Conductive TiN as a catalyst for sulfur cathode is expected to improve the reaction activity between lithium and sulfur under high current densities. Further, the ALD technique facilitates uniform thin film deposition that is conformal to the substrate with angstrom level control over film thickness. In this research, ALD TiO$_2$ derived TiN nanoparticles are demonstrated to have uniform distribution on porous carbon powder, acting as a catalyst to effectively support sulfur during the Li-S electrochemical reaction [19-21].

4.2 Experimental

**Materials synthesis:** TiN is synthesis via post treatment of atomic layer deposited (ALD) TiO$_2$ on commercial mesoporous carbon (KJE C600). Atomic layer deposition was conducted in a Savannah 100 ALD system (Cambridge Nanotech, USA). ALD TiO$_2$ coating was grown on the carbon at 100 °C by using titanium isopropoxide and H$_2$O as precursors. The as-prepared TiO$_2$@carbon then treated under 900 °C with ammonia and hydrogen to reduce to TiN@carbon, as shown in Figure 1. The formed TiN@carbon mixed with sulfur powder and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 12 h. The pristine sulfur-carbon composite is synthesized via same one-step thermal procedure as a reference sample. The obtained sulfur-carbon black composites maintained 65 wt% sulfur load.

**Physical characterization:** The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV. CR-2032 type coin cells were assembled in argon filled glove box. Thermo gravimetric analysis (TGA) was carried out on a TA SDT Q600 in an N$_2$ atmosphere from room temperature to 700 °C at a rate of 10 °C/min.

**Electrochemical characterization:** The coin-type cells consisted of Li metal as anode, a separator, and as-prepared electrode as cathode. The electrolyte was composed of 1M LiTSFI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio.
Cyclic voltammograms and electrochemical impedance spectra (EIS) were collected on a versatile multichannel potentiostation 3/Z (VMP3) under scanning rate of 0.1 mV s\(^{-1}\) between 1.0 V- 3.0 V (vs. Li/Li\(^+\)). Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V-3.0 V (vs. Li/Li\(^+\)) at room temperature using an Arbin BT-2000 Battery Tester.

### 4.3 Results and Discussion

As shown in **Figure 4.1**, ALD TiO\(_2\) thin film was deposited on commercial carbon black (KJ EC600, US) with the use titanium isopropoxide (TTIP) and water as precursors (detailed in experimental section). Following this, the as-prepared ALD-TiO\(_2\)@carbon then was then treated with ammonia under high temperature to obtain TiN@carbon [15, 22]. During the high temperature treatment, the conformal TiO\(_2\) thin film aggregates into nanoparticles and is reduced to TiN via ammonia. As show in **Figure S4.4**, the XRD pattern indicates the presence of a pure TiN phase following high temperature treatment, suggesting that the ALD-TiO\(_2\) is has been successfully altered into TiN composites. **Figure 4.2a** shows the FE-SEM image of as-prepared TiN@carbon nanocomposites (TNC) and displays the presence of nanoparticle agglomerates within the range of 40-60 nm, similar to the size of pristine porous carbon nanoparticles. As seen in **Figure 4.2b-d**, the existence of Ti and N elements are verified through the use of FESEM-EDS, indicating uniform distribution of TiN nanocomposites. Besides, TEM-EDS further confirms the uniform distribution of TiN on the carbon power. As shown in **Figure 4.2e**, elemental spectra comparison reveals that the white spots are TiN nanoparticles with particle size around 2 nm [23-25]. Confirmed from FESEM-EDS and TEM-EDS results, TiN nanoparticles are deposited very uniformly on carbon nanoparticles via ALD, which facilitates effective contact with sulfur in the subsequent synthetic steps (**Figure 4.1**). To prepare C-S composites, a one-step thermal process is employed to prepare sulfur/TiN@carbon composites (S/TNC) and sulfur/carbon composites (S/C). As shown in **Figure S4.1**, the sulfur load of as-prepared sulfur composites is about 65 wt\%, and is confirmed through the use of TGA.
Figure 4.1 Schematic diagram of synthesis steps for S/TiN@C.

Figure 4.2 (a,b) SEM images of TiN@carbon, (c,d) corresponding EDX mapping spectra of Ti and N element of (b); (e) TEM image of TiN@carbon; and (f) TEM-EDX element analysis of corresponding areas in (e).
To demonstrate the catalytic effect of TiN in Li-S systems, electrochemical characterization was conducted. **Figure 4.3a** shows the cycle performance of sulfur cathodes under various current densities. Compared to the bare S/C cathode, the S/TNC cathode displayed significant improvement to both cycling capacity and coulombic efficiency. The initial discharge capacity is about 1350 mAh g\(^{-1}\) at 800 mA g\(^{-1}\). After 100
cycles, the discharge capacity was found to be 900 mAh g\(^{-1}\), which is over 200 \% times the capacity found for the bare S/C cathode following 100 cycles (450 mAh g\(^{-1}\)). Further, S/TNC also showed impressive cycle performance under high current density. Even at 6400 mA g\(^{-1}\), the discharge capacity of the S/TNC maintained over 700 mAh g\(^{-1}\) after 100 cycles. Moreover, good rate performance under varies current densities was also carried demonstrate, as shown in Figure S4.2a. The improved battery cycle life illustrates that TiN as a catalyst facilitates the activity of Li-S redox reaction.

To further reveal the catalytic mechanism of TiN in Li-S system, cyclic voltammetry was measured using a sweep rate of 0.1 mV s\(^{-1}\) as shown in Figure 4.3b. Both of S/TNC and S/C cathodes showed typical Li-S redox reactions in the CV profile. During the cathodic process, two peaks appear at 2.3 V and 2.1 V, corresponding to \(S_8\) molecule being reduced to long chain polysulfides, and further reduced to short chain polysulfides. The anodic process shows one peak at 2.4 V, corresponding to \(Li_2S_2\) or \(Li_2S\) being oxidized to sulfur molecule [4, 12, 26]. The CV peaks are also in agreement with the potential plateaus of discharge-charge curves, as shown in Figure S4.2b. Peak intensity of normalized CV profiles reflects the electrochemical reaction activity of the battery. The anodic peaks of S/C is much stronger than that of cathodic peaks in the CV profile, indicating a serious “shuttle effect” accompanied with the multiple electrochemical reactions. In contrast, the intensity of the anodic and cathodic peaks of S/TNC is comparable, implying that the “shuttle effect” is being alleviated through the catalytic effects of TiN. Besides, S/TNC displays a much slower decay than that of S/C in term of cathodic peak intensity in the first three CV cycles, which is consistent with the cycling performance obtained. The CV profile reflects that TiN catalyst effectively promotes the Li-S electrochemical reaction. The catalyst facilitates the oxidation of polysulfide during charging process and effectively relieves the “shuttle effect”; and also is favorable to the reduction process of sulfur during discharging process, leading to increased utilization of sulfur active material.
Figure 4.4 FE-SEM images of (a) S/C and (b) S/TNC electrodes after battery test; (c) Li elemental mass ratio in electrodes estimated by ICP-AES analysis.

Cycled batteries were further measured to confirm the proposed mechanism of catalytic TiN. Figure 4.4a and 4b are FESEM images of as-prepared sulfur electrodes after 20 charge-discharge cycles. The surface of the S/C electrode is covered by a thick deposition, resulting from dissolved polysulfides out of the carbon matrix resulting in the formation of discharge product on the electrode surface [7, 27]. However, S/TNC displays fewer discharge products deposited on the surface, confirming a highly reversible Li-S redox reaction with TiN supported carbon host. To get further insight into the discharge product depositing process, electrical impedance spectra were obtained and is shown in Figure S4.3. The impedance spectra of S/C and S/TNC consists of two semi-circles and one line. The semicircle in the mid frequency region is related to charge-transfer processes occurring the interface between the cathode and the electrolyte, typically resulting in the formation of an insulating lithium sulfide layer (Li₂S/Li₂S₂) [12, 28]. The diameter of the semicircle in the EIS spectra reflects the resistance of the interface charge-transfer process. Interestingly, the resistance from the Li₂S insulating layer for the S/TNC cathode is much smaller than that found for the S/C cathode. Combined with the morphology of electrodes after cycling, these results demonstrate that TiN catalyst effectively reduced the polysulfides dissolution and avoids the buildup of insulated discharge products aggregation.
To further reveal the catalytic mechanism of TiN towards the reversibility of Li-S batteries, inductively coupled plasma atomic emission spectroscopy (ICP-AES) are utilized, as shown in Figure 4.4d. ICP-AES was employed to quantitatively examine the ratio of irreversible product in the total mass of cathodes. The results presented in Figure 4.4d indicates that the Li content of S/C electrode is much stronger than that of S/TNC, which implied that S/C cathode had big amount of irreversible discharge products after cycling. Furthermore, the low value of Li content in S/TNC cathode confirmed TiN can effectively promote the reversibility of Li-S redox reaction, which is consistent with the obtained electrochemical results.

4.4 Conclusion

In summary, for the first time, titanium nitride is applied as a catalyst in Li-S batteries via an ALD synthetic process. From physical characterization, the ALD approach demonstrated uniform deposition of nanoscale metal oxide which was subsequently altered into the active nitride catalyst on carbon nanoparticles. As confirmed from electrochemical characterizations, TiN improves the reversibility of the Li-S electrochemical reaction and increases the utilization of sulfur during cycling. Furthermore, the use of this electrode under high current densities demonstrates that the TiN supported sulfur cathodes can significantly improve cycle life, displaying 700 mAh g\(^{-1}\) after 100 cycles under 6400 mA g\(^{-1}\). The catalytic mechanism of TiN on Li-S system is still under research. This research gives new sight on the use of metal nitride catalyst for high rate Li-S batteries, and the synthesis of metal oxide or metal nitride catalysts supported on carbon materials via ALD technology opens a new direction for Li-S, Li-ion, and other energy storage systems.

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References


Supporting Information

Figure S4.1 TGA profiles of S/TNC and S/C composites
Figure S4.2 (a) Typical discharge-charge profile and (b) rate performance of S/TNC cathode
Figure S4.3 EIS spectra of S/TNC and S/C (a) before and (b) after battery cycling test.

Figure S4.4 XRD pattern of TiN@ carbon.
Chapter 5

5 Tunable porous structure of metal organic framework derived carbon and the application in lithium sulfur batteries

Carbon materials are the most employed host materials for sulfur cathodes due to the high conductivity and light weight. Except of high conductivity, nanoporous structure is another crucial factor of carbon hosts for sulfur cathodes. As reported reference, different porous structures directly result in different reaction routes of lithium sulfur (Li-S) electrochemical process. For instance, micropore (< 2 nm) enables to store short chain sulfur molecule and the electrochemical reaction can be considered as all-solid-phase process. On the other hand, $S_8$ ring molecule can be stored in the mesoporous structure, which undergoes a liquid-solid dual-phase electrochemical reaction of Li-S batteries. Furthermore, the nanoporous structure also determines the penetration of electrolyte and utilization of sulfur from cathode part. Therefore, optimization of porous structure of carbon materials for sulfur active material with high utilization is crucial in design of sulfur cathode.

Metal organic framework derived carbon (MOF-C) is a novel material of carbon family. It obtains unique morphology and ultra-high surface area and porous volume in the carbon cage. Besides, the MOF-C enables to obtain enriched heteroatoms doping from the MOFs. Based on aforementioned properties, MOF-Cs are very suitable as carbon hosts for sulfur cathodes.

In this chapter, as-prepared MOF-Cs are synthesized as carbon hosts for sulfur cathode. By using facile gas-phase annealing treatment, the MOF-Cs are tailored with different nanoporous structure. Detailed electrochemical characterization of sulfur cathodes with as-prepared MOF-Cs is carried out, and mechanisms of the different porous structure are stated.

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5.1 Introduction

Seeking for high energy storage systems is an inevitable challenge accompanied with the depletion of fossil energy [1-3]. Although the state-of-art Li-ion batteries have been successfully commercialized for portable electronics applications, they still cannot meet the requirements of electric vehicles (EVs) or hybrid electric vehicles (HEVs) in terms of energy density [4-6]. Li-S batteries are one of the promising candidates due to their inherently ultrahigh theoretic capacity and energy density, which are nearly five times greater than commercial Li-ion batteries [7-9]. Sulfur itself also possesses features such as environmental benignity, economy, and sustainability [7-9]. Within this context, Li-S batteries are regarded as one of the next generation batteries for EVs and HEVs. However, sulfur cathodes are still impeded by many issues that need to be further elucidated [10-12]. Low utilization of sulfur cathodes arises in electrochemical reaction due to the insulating nature of sulfur. More seriously, poor reversibility of sulfur due to the dissolution of polysulfides results in limited cycle life of Li-S batteries [10-12].

Nanoporous carbon materials are used as sulfur hosts, which dominate the performance of Li-S batteries [13-15]. An ideal nanoporous carbon material should obtain following characteristics [13-15]: (1) high electric conductivity to improve the insulating nature of sulfur; (2) high pore volume to maintain high loading of sulfur; (3) fluent channels enabling sufficient electrolyte infiltration (Li-ions insertion and extraction); and (4) effective sorption to prevent polysulfides from dissolution. Further, it has been reported that the “small sulfur molecule” (short chain sulfur molecule) in micropores performed through different electrochemical processes in Li-S systems [16, 17]. Therefore, designing advanced carbon materials with desirable pore distribution as a sulfur host is one of the key issues in Li-S battery systems.

Very recently, metal organic framework-derived carbon (MOF-C) has been regarded as a new and popular family of porous carbon materials inspired by the ordered structure, high surface area, and unique morphology of MOFs [18-20]. To date, several MOF structures, such as zinc based MOF-5, zeolitic imidazolate framework ZIF-8, and Al-based porous coordination polymer Al-PCP have been reported as precursors to create nanoporous
carbon [21-25]. The advantages of MOF-C including microporous nanostructure, high surface area, large pore volume, specific morphology, and inherent heteroatoms doping facilitate various applications of MOF-C in gas storage, catalyst, solar cell, fuel cell, and Li-based batteries [26-30]. Actually, different energy storage systems need various porous structures of hosts [31, 32]. For instance, gas storage system needs fitted microporous structure, while metal-air batteries prefer large porous structure. However, very few researches have studied the control of porous structure of MOF-C from fitted microporous structure (< 2 nm) to hierarchically mesoporous structure (2-50 nm) and, especially, to large porous structure (> 100 nm) because the complicated synthetic process of large-pore MOF makes it hard to obtain large porous carbon from directly carbonized MOFs [33-35].

For the first time, we report a facile in-situ ammonia treatment approach aimed at producing various porous structures of MOF derived carbon ranging from micropores to hierarchically mesopores. Different from directly attempting some MOF-Cs in application, this strategy enables to design varies of porous structure of MOF-C from one starting material. Further, the ammonia treated MOF-C as carbon host shows an impressive improvement on sulfur cathodes, which performed twice higher discharge capacity retention than that of the pristine MOF-C sample. Cyclic voltammetry and other physical characterizations demonstrated that ammonia treatment can tailor the MOF-C into proper nanostructure for sulfur molecule deposition and detailed electrochemical mechanisms are proposed in this study. This research sheds light to design MOF-C materials with controlled nanostructure not only for Li-S batteries, but also for expanded applications in different energy storage systems.

5.2 Experimental

5.2.1 Preparation of ZIF-8 derived carbon and ammonia treated carbon

The synthesis of ZIF-8 derived carbon follows the approach reported by Xu’s group [22]. Typically, commercial zeolite-type metal-organic framework ZIF-8 (Basolite Z1200, Sigma-Aldrich) and furfuryl alcohol (FA, Sigma-Aldrich) were used as the starting materials. FA was firstly introduced into ZIF-8 to obtain FA/ZIF-8 composites under an
evacuated environment. The FA/ZIF-8 composites were then transferred into a furnace under Ar atmosphere and heated in a program at 80 °C for 24 h, then at 150 °C for 6 h, and finally at 1000 °C for 8 h to obtain ZIF-8 derived carbon (C-ZIF). The obtained C-ZIF was then in-situ treated under ammonia atmosphere at 1050 °C for 3, 5, and 7 min. The obtained samples are referred as N3-C, N5-C, and N7-C.

5.2.2 Preparation of sulfur-carbon composite

Sulfur-carbon composites (S/C) were synthesized via a two-step thermal-treatment procedure. The as-prepared carbon materials (C-ZIF, N3-C, N5-C, and N7-C) were mixed with sulfur powders (> 99.5%, Sigma-Aldrich) and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and 300 °C for 3 h to obtain the S/C composites. A reference S/C composites sample using commercial porous carbon (KJ-600, US) as carbon host is also synthesized following same procedure. As-prepared sulfur-carbon black composites maintained 60-65 wt% sulfur load from TGA results.

5.2.3 Physical and Electrochemical Characterization

The morphologies and structure of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV, high-resolution transmission electron microscopy (HRTEM) (JEOL 2010 FEG) equipped with energy dispersive spectroscopy (EDS), and X-ray diffraction system (XRD) (Bruker D8 Advance, Cu Kα X-ray source). Thermo gravimetric analysis (TGA) was carried out on a TA SDT Q600 in an N₂ atmosphere from room temperature to 700 °C at a rate of 10 °C/min. Raman scattering (RS) spectra was obtained using a HORIBA Scientific LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser. CR-2032 type coin cells were assembled in argon filled glove box. The coin-type cells consisted of Li metal as anode, a separator, and as-prepared electrode as cathode. The electrolyte was composed of 1M LiTFSI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under scanning rate of 0.1 mV s⁻¹ between 1.0 V- 3.0 V (vs. Li/Li⁺). Charge-
discharge characteristics were galvanostatically tested in the range of 1.0 V-3.0 V (vs. Li/Li⁺) at room temperature using an Arbin BT-2000 Battery Tester.

5.3 Results and discussion

As shown in Figure 5.1, commercial ZIF-8 was immersed in furfuryl alcohol (FA) which allows FA penetrating into ZIF-8 framework and producing extra surface area for ZIF-8 derived porous carbon (C-ZIF) [22]. The FA/ZIF-8 composites were then annealed under a delicate pyrolyzing program to vaporize the zinc metal and form porous carbon material C-ZIF. During the annealing process, C-ZIF was simultaneously treated by ammonia for different lengths of time to build various porous structure, which is denoted as Nx-C (x= 3 min, 5 min, 7 min). By using as-prepared porous carbon as hosts, sulfur was filled into the Nx-C materials to build S/C composites and are proposed to form different polyatomic molecules in porous Nx-C, which is aimed to improve the Li-S batteries performance via optimizing MOF-C hosts.

Figure 5.1 Synthetic steps of MOF-C and S/MOF-C composites, and proposed mechanism of porous structure formation and sulfur deposition.
Figure 5.2 FE-SEM images of: (a) ZIF-8 (b) C-ZIF, directly carbonized from ZIF-8; (c) N3-C, NH$_3$ treated C-ZIF in 3 mins; (d) N7-C is NH$_3$ treated in 7 mins

Understanding the physical properties of porous carbon, especially the ammonia effect on C-ZIF is crucial in this research. FE-SEM images (Figure 5.2b-d) confirmed that all of the as-prepared carbon materials can preserve the unique morphology of ZIF-8 even after high temperature annealing procedure. The particle size of MOF-Cs is about 100-150 nm in average. Compared with commercial ZIF-8 (Figure 5.2a), the surface of as-prepared carbon materials become rough and the particles are shrunken, corresponding to the zinc evaporation at high temperature and porous structure formation. XRD patterns and Raman spectra further confirmed the successful formation of carbon from ZIF-8. XRD patterns (Figure S5.1) of as-prepared carbon materials all showed two board peaks at around 24$^\circ$ and 44$^\circ$ which are attributed to the (002) and (101) diffractions of carbon [36, 37]. The two board peaks refer to the partially graphitic carbon, confirming that ZIF-8 (Figure S5.2a) was transformed to carbon after annealing and ammonia treating procedure. Raman spectra are acquired to investigate the graphitic order of the as-prepared carbon materials. As shown in Figure 5.3a, all of the Raman spectra are composed of D (1350 cm$^{-1}$) and G band (1590 cm$^{-1}$) which are associated with the disordered and graphitic carbon, respectively [38, 39]. Interestingly, the intensity ratio between D and G band of as-prepared carbon are gradually changed along with the time of ammonia treatment. The G band intensity of C-ZIF is higher than D band (I$_D$/I$_G$ <1), which indicates that C-ZIF forms high ratio of graphitic carbon phase after high temperature annealing process. However, the intensities of D band rise with the increasing ammonia treating time, especially in N7-C with the
longest ammonia treating time, the D band intensity is higher than G band (I_D/I_G > 1). The increasing D band intensity indicates that ammonia etched the carbon under high temperature and resulted in the formation of more defect sites inside of the carbon. Thus it can be proposed that ammonia treatment will change the composition and structural properties of C-ZIF.

Figure 5.3 (a) Raman spectra, (b) nitrogen adsorption/desorption isotherm, and (c) surface area and pore volume distribution of as-prepared MOF-Cs.

To further understand the ammonia effect on surface property of MOF-Cs, Figure 5.3b, Figure 5.3c, and Figure S5.3 illustrate the pore volume distribution and surface area of as-prepared carbon materials. Nitrogen absorption-desorption isotherms demonstrate that ZIF-C is composed by enriched micropores and NH₃ treatment enables to modify the surface area and porous structure of MOF-Cs. As shown in Figure 5.3c, the surface area of ammonia treated carbon materials is increased compared with C-ZIF (1500 m² g⁻¹). In
particular, N3-C rises to over 1900 m² g⁻¹ with 3-min NH₃ treatment. The increase of surface area demonstrates that NH₃ etches the C-ZIF and contributes extra space for the carbon materials. According to BJH desorption cumulative pore volume and t-plot microporous volume statistics, the stacked column chart embodies the hierarchically nanoporous structure distribution in terms of NH₃ treating time. C-ZIF is mainly composed with micropores. The micropores are then enlarged into small mesopores when treated by NH₃ in 3 minutes (N3-C). With longer NH₃ treating time, the small mesopores are further enlarged to large mesopores and are also accompanied with many new micropores formation. The carbon material with 7-min ammonia treatment (N7-C) is composed with various nanostructures and the pore volume rose to 1.3 cm³ g⁻¹, which is twice of the C-ZIF. Compared with the mono-microporous structured C-ZIF, NH₃ treatment facilitates the enlargement of the pore volume and builds hierarchically nanoporous structure on the MOF-derived carbon. Based on the characterizations mentioned above, we successfully use in-situ ammonia treatment to design different porous carbon derived from ZIF-8.

**Figure 5.4** (a) SEM image and (b-d) STEM-EDX elemental mapping of S/N3-C composites.

S/MOF-C composite were synthesized via two-step heating process to allow sulfur uniformly infill into the carbon matrix. The diffusion of sulfur directly impacts the
conductivity of C/S composites and sulfur cathode performance. As shown in Figure 5.4 and Figure S5.4, no obvious isolated sulfur particles of S/N3-C composite were observed from FESEM and TEM images, and energy dispersive X-ray spectroscopy under scanning transmission electron microscopy (STEM-EDX) demonstrates very uniform sulfur distribution in MOF-derived carbon matrix (Figure 5.4b-d), which facilitates the effective utilization of sulfur in the following electrochemical processes.

**Figure 5.5** Cycle performance of sulfur cathodes with different MOF-C as hosts.

**Figure 5.5** gives a comparison of the cycle performance among S/MOF-C cathodes. Interestingly, the MOF-Cs as carbon hosts demonstrated significant differences on the performance of sulfur cathodes. S/N3-C showed the best cycle performance that the initial discharge capacity is about 1500 mAh g\(^{-1}\), indicating a high sulfur utilization. After 100 cycles, the discharge capacity retention is about 800 mAh g\(^{-1}\). However, S/C-ZIF and S/N7-C performed low initial capacity and fast decay during cycling. The capacity of S/N3-C after 100 cycles is twice higher than that of S/C-ZIF and S/N7-C cathodes, which indicates that a proper ammonia treatment effectively optimizes the nanostructure of carbon for sulfur cathode. Besides, N3-C shows improved Coulombic efficiency compared with C-ZIF and N7-C, further confirming that the optimized MOF-C facilitates high utilization of active material and stability of Li-S batteries during cycling. Since MOF-C is very novel carbon host in Li-S batteries, we also make a comparison of Li-S batteries performance between MOF-C and commercial porous carbon (KJ-600) as hosts, as shown in Figure
S5.5. Impressively, N3-C shows better performance in Li-S batteries, which further demonstrates MOF-C with designed porous structure is a promising carbon material in energy storage applications. The detailed electrochemical process and proposed mechanism of MOF-C on Li-S batteries are discussed as following.

**Figure 5.6** Cyclic voltammetry curves of sulfur cathodes with as-prepared carbon materials, and proposed mechanisms of corresponded sulfur cathodic processes.

In Li-S batteries, porous structure of carbon host is closely bounded to the electrochemical performance of sulfur/carbon composite (S/C) cathodes. The pore width of carbon
determines the distribution and chemical formulas of sulfur in carbon host, the infiltration of electrolyte in sulfur cathodes, as well as the trapping capability of dissolved polysulfides. Figure 5.6 shows the cyclic voltammetry (CV) curves of as-prepared S/C cathodes and the corresponding electrochemical reactions. Interestingly, the sulfur cathodes express different electrochemical reacting processes. C-ZIF shows three cathodic peaks with two sharp ones at 2.3 V and 2.1 V, and one broad peak at 1.4 V in the first cathodic process. The peaks at 2.3 V and 2.1 V correspond to the sulfur-lithium polysulfide-lithium sulfide multi-step reaction mechanism (referred as normal sulfur based on solution phase) [17, 40, 41]. The broad peak at 1.4 V, interestingly, corresponds to the lithiation of small sulfur molecules trapped in micropores [42, 43]. The “small sulfur molecule” phenomenon is the sulfur molecules existed as short chain formation ($S_{4}^{2-}$, $S_{3}^{2-}$) when sulfur is diffused into micropores. Lithiated “small sulfur” reaction is considered to occur under solid phase, leading to lower cathodic peak (1.5 V) compared with the solution phase reaction (2.1 V) [44, 45]. However, this “small sulfur molecule” electrochemical process is irreversible that the peak at 1.4 V almost disappears in the second and third cycles. Besides, the intensity of the cathodic peak decreases rapidly upon cycling, which may be attributed to the low infiltration of electrolyte in microporous-structured C-ZIF. Interestingly, the S/N3-C shows very stable and highly reversible electrochemical processes. The sulfur cathode only shows two cathodic peaks at 2.3 V and 2.1 V, corresponding to normal Li-S electrochemical reaction process. The intensity of both cathodic and anodic peaks in the first three cycles are very sharp and stable, corresponding to high electrochemical activity and reversibility of sulfur cathodes with N3-C host. S/N7-C displays a strong cathodic peak at around 1.5 V, which implies that a drastic amount of sulfur was “small sulfur molecule” in S/N7-C composites. Importantly, the three cathodic peak processes from S/N7-C cathode demonstrate the different electrochemical routes of sulfur in different porous structures, referring as solid phase and solution phase electrochemical transformation, separately. However, most of the small sulfur molecules are irreversible in subsequent cycles which results in serious loss of active sulfur materials in the following redox reactions. Besides, S/N7-C shows an ultra-high anodic peak, indicating a serious “shuttle effect” during electrochemical process. Electrochemical performance of S/N5-C shows a consistent trend with S/N7-C, as shown in Figure S5.5, which expresses a significant ratio
of irreversible “small sulfur” electrochemical reaction and serious “shuttle effect”. To summarize, comparing with Nx-C, the pore volume and average pore width of original C-ZIF is too small to maintain the sulfur in Li-S batteries, which displays an insufficient electrochemical reaction. Proper NH$_3$ treated N3-C carbon demonstrates a proper porous structure for Li-S systems that enables sufficient electrolyte infiltration and also maintains sulfur in carbon matrix, leading to high reactivity and reversibility of Li-S redox reaction [46]. On the other hand, extending ammonia treating time from 3 min to 7 min will further etch the carbon, leading to enlarged mesopores as well as new micropores formation, as shown in the proposed mechanism of pore formation in Figure 5.1. The broad pore width of N5-C and N7-C results in a deteriorative Li-S electrochemical process from the CV curves, which is due to the drastic amount of irreversible “small sulfur molecule” and serious “shuttle effect” from dissolved polysulfides.

5.4 Conclusion

In summary, hierarchically porous MOF-derived carbon materials with controllable pore distribution have been successfully synthesized via in-situ ammonia treatment during annealing process. The enriched micropores of original C-ZIF are stepwise enlarged into mesopores (2-10 nm) and even large mesopores (> 10 nm) with increasing ammonia treating timespan. Electrochemical performance and proposed mechanism of S/MOF-C in Li-S batteries are investigated. The multi-phase electrochemical reaction processes of sulfur have been demonstrated based on hybrid porous MOF-C. More importantly, the hybrid porous structure of MOF-C with ammonia treatment demonstrated about 800 mAh g$^{-1}$ of discharge capacity over 100 cycles, which is over two times higher than pristine ZIF-8 derived carbon. The promising Li-S battery performance illustrates the ammonia treatment approach expands the application of MOF-C in batteries. Unlike previous literature which directly pyrolysis of MOF and blind attempt in some applications, this strategy enables to design varies porous structure of MOF-C for specific energy storage applications. In perspective, the ammonia treatment enables the control of various nanoporous structures on MOF-C, which carves the potential applications for MOFs and optimized MOF-C materials in various energy storage systems.
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References


Supporting information

**Figure S5. 1** (a) XRD pattern and (b) Raman spectrum of ZIF-8.

**Figure S5. 2** XRD of as-prepared MOF-C materials
Figure S5. 3 Pore size distribution of as-prepared MOF-Cs and proposed schematic diagram of MOF-C/S composites.
Figure S5. 4 HRTEM image of a single particle of S/N3-C composites.

Figure S5. 5 Cycle performance of N3-C/S composite and commercial C/S composite under 0.1 C.
Figure S5.6 Physical characterizations of N5-C and electrochemical performance in S/N5-C composite. (a) SEM images, (b) Raman spectrum, (c) CV profiles, (d) pore distribution, and (e) cycle performance.
Figure S5. 7 Discharge-charge curves of S/C composites.

Figure S5. 8 TGA profiles of as-prepared C-S composites.
**Figure S5. 9** FE-SEM image of S/N3-C electrode after cycling test

**Figure S5. 10** EIS spectra of S/N3-C electrode before and after cycling test.
Chapter 6

6 Nanoscale stabilization of Li-sulfur batteries by atomic layer deposited Al$_2$O$_3$

Dissolution of polysulfides is one of crucial challenges of sulfur cathodes. The dissolved polysulfides will trigger “shuttle effect” which results in serious loss of sulfur active material and also corrosion of lithium anode. Except of encapsulated sulfur in carbon host, coating is another popular strategy employed for sulfur cathodes to prevent the dissolution of polysulfides. An ideal coating material should be (1) uniform and integrate to protect sulfur cathode; (2) ultrathin to allow Li-ion smooth penetration; and (3) excellent mechanical properties to accommodate the volume expansion of sulfur cathode with long cycle life.

Atomic layer deposition enables to grow metal oxide thin film with precisely controlled under atomic level. Due to the self-limited binary reaction, the ALD thin film enables to penetrate through the whole electrode and deposit very uniform on substrate, which gives effective protection for sulfur cathode. Further, the ultrathin film facilitates the Li-ion smooth penetration, which maintains the conductivity of electrode network.

In this chapter, ALD Al$_2$O$_3$ is employed as coating materials for sulfur based electrode. The research studied the thickness effect of ALD Al$_2$O$_3$ coating on sulfur cathode with electrochemical characterizations of Li-S batteries. Synchrotron based X-ray study is also carried out in this research to demonstrate the Al$_2$O$_3$ coating effect for sulfur cathodes.

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6.1 Introduction

Li-sulfur batteries have been considered as one of the most promising power storage systems for electric vehicles, owing to their overwhelming advantages in specific capacity and energy density [1-5]. Moreover, sulfur is attractive in its low cost, abundance, and environmental benignity [1-5]. Nevertheless, the present Li-sulfur batteries suffer from two major problems, which seriously hinder their commercial application [6-12]. One major issue is the inherent insulating nature of sulfur and discharge products Li$_2$S$_n$ (n<2), which greatly limits the performance of Li-sulfur batteries [6-12]. Another issue is that polysulfide species, the dissolved intermediate product, will migrate between two electrodes and chemically react with lithium metal or sulfur cathode directly, leading to a drastic corrosion of lithium metal and loss of sulfur active material. This phenomenon is known as “shuttle effect” [6-12].

To improve the conductivity of sulfur cathodes, the prevailing strategies are addition of carbon materials, which has made efforts to the prosperity of Li-S batteries [6-14]. On the other hand, it has been widely accepted that the “shuttle effect” could be alleviated by coating S-based composites with conductive polymer [14, 15], metal oxides [16, 17], as well as graphene and carbon papers [13, 18-21] et al. Atomic layer deposition (ALD) is a thin film depositing technique which is featured with conformal growth, precisely controllable thickness, as well as fast and facile operating processes [22-25]. Recently, ALD has been exerted to coat the electrode materials in Li-ion batteries (LIBs), and proven to be effective to prevent unexpected side reactions and improve the performance of LIBs. However, the application of ALD coating Li-sulfur batteries has rarely been unveiled [26-28]. Yushin et al. [26] reported that Al$_2$O$_3$ coating by plasma-enhanced ALD could improve the cycling performance of Li-S batteries, owing to the suppressed deposition of Li2S on electrodes by Al$_2$O$_3$ coating. Another research by Wang et al. [27] employed ALD-Al$_2$O$_3$ coated carbon paper as a reactivation layer between sulfur cathode and separator in cell, constructing a novel configuration for Li-sulfur batteries. However, detailed Al$_2$O$_3$ coating effects and reaction mechanisms have not been carried out.
Herein, the influence of Al$_2$O$_3$ coatings with different thicknesses by ALD on the performance of sulfur-based electrodes is studied in detail. It is found that 2-cycle Al$_2$O$_3$ coating (~0.2 nm in thickness) could effectively improve the performance of Li-S batteries. The underlying reason for the performance improvement was investigated by synchrotron-based X-ray photoelectron spectroscopy (XPS), and a working mechanism was proposed. It is found that AlF$_3$/LiAlO$_2$ ionic conductive layer is formed during cell operation derived from Al$_2$O$_3$ layer. The conformal ALD coating facilitates both the confinement of polysulfide and the high utilization of sulfur active material, leading to impressive electrochemical performance of Li-sulfur batteries.

6.2 Experimental

6.2.1 Preparation of carbon-sulfur composite and Al$_2$O$_3$ ALD coating on carbon-sulfur electrode

Commercial carbon black was mixed with sulfur powder and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained sulfur-carbon black composites maintained 65 wt% sulfur load. The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 70:20:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum. Atomic layer deposition was conducted in a Savannah 100 ALD system (Cambridge Nanotech, USA). ALD Al$_2$O$_3$ coating was grown on the C/S electrode at 100 °C by using trimethylaluminium and H$_2$O as precursors. To obtain Al$_2$O$_3$ coatings with different thicknesses, 2-, 5-, 10-, and 20-cycle Al$_2$O$_3$ by ALD were conducted directly on sulfur-carbon electrodes at 100 °C using TMA and H$_2$O as precursors (see details in ESI). On the basis of ALD mechanism, the thickness of coating layer should be linearly increased with stepwise ALD reactions. The thicknesses of 2-cycle and 20-cycle ALD coating are about 0.2 and 3 nm theoretically [22, 29].

6.2.2 Physical and electrochemical characterization

The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV. CR-2032 type coin cells were
assembled in argon filled glove box. The coin-type cells consisted of Li metal as anode, a separator, and as-prepared electrode as cathode. The electrolyte was composed of 1M LiTSFI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under scanning rate of 0.1 mV/s between 1.0 V - 3.0 V (vs. Li/Li⁺). Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V-3.0 V (vs. Li/Li⁺) at room temperature using an Arbin BT-2000 Battery Tester. X-ray photoelectron spectroscopy (XPS) experiments on the Al 2p were conducted on the variable line spacing plane grating monochromator (VLS PGM) beamline at the Canadian Light Source (CLS), located at the University of Saskatchewan in Saskatoon. Thermogravimetric analysis (TGA) was carried out on a TA SDT Q600 in an N₂ atmosphere from room temperature to 700 °C at a rate of 10 °C/min.

6.3 Results and Discussion

Figure 6.1 shows the FE-SEM, and elemental mapping images of C/S composites with 2-cycle Al₂O₃ coating. Uniform aluminum elemental mapping of electrode is presented under micrometer magnitude, indicating the conformal Al₂O₃ ALD coating growth on the surface of electrode. Typical morphologies and Al elemental mapping images of 5, 10, and 20-cycle are shown in Figure S6.2. The typical morphologies of these four samples with Al₂O₃ coating are agglomerated nanoparticles within a size of 30-40 nm, comparable with bare C/S electrode (Figure S6.3).

Figure 6.1 (a, b, c) FE-SEM, elemental mapping images and (d) FE-SEM image under high magnification of C/S composites with 2-cycle Al₂O₃ coating.
Figure 6.2 (a) Typical cyclic voltammograms and (b) cycle performance of sulfur cathodes with and without Al$_2$O$_3$ coating.

Electrochemical performances of C/S electrodes with and without Al$_2$O$_3$ coating are illustrated in Figure 6.2. It is well known that the peak position and area of CV profiles are contingent on the conductivity of electrodes, the utilization of active materials, and the reversibility of batteries [30, 31]. As shown in Figure 6.2a, all the electrodes present two cathodic peaks at 2.3 V and 2.1 V, and one anodic peak at 2.4 V, both of which are consistent with regular Li-sulfur CV profiles. Interestingly, compared with bare C/S electrode, 2-cycle and 5-cycle Al$_2$O$_3$ coated electrodes exhibit lower intensity of anodic peaks, but comparable intensity of cathodic peaks. This phenomenon strongly suggests that ultrathin Al$_2$O$_3$ coating relieves the “shuttle effect” with the conductivity of coated electrodes preserved. On the other hand, in CV profiles, the normalized sweeping areas of
10-cycle and 20-cycle Al₂O₃ electrodes are much smaller than those of other samples. The reason is that the thicker Al₂O₃ layers block the Li-ion diffusion, leading to reduced sulfur utilization in cell operation.

Figure 6.3 FE-SEM images of (a) pristine carbon-sulfur electrode, (b) 5-cycle, and (c) 20-cycle Al₂O₃ coated electrodes after 30 discharge-charge cycles.

Cycling performances of the electrodes with and without Al₂O₃ coatings under 0.1 C (160 mA g⁻¹) are presented in Figure 6.2b. The pristine C/S composites show an unstable cycling performance with very low coulombic efficiency (stabilized at 70 %). After 70 cycles, the discharge capacity only remains 460 mAh g⁻¹. In contrast, the 2-cycle Al₂O₃ coated C/S cathode exhibits an improved cycling performance. The battery during initial 20 cycles is more stable than that of the bare one. After 70 cycles, the discharge capacity keeps 640 mAh g⁻¹, indicating that the ultrathin Al₂O₃ coating can significantly improve the performance of sulfur cathode. On the other hand, cycling performances of 10-cycle and 20-cycle Al₂O₃ are not as good as 2-cycle. Although 20-cycle Al₂O₃ electrode displays an enhanced cycling stability, the first and 10th cycle discharge capacities are only about 1099 and 590 mAh g⁻¹, corresponding to limited sulfur utilization, well consisted with CV profiles.
Figure 6.4 Synchrotron based Al 2p XPS spectra of (a) electrodes after cycling and (b) deconvolution of each spectrum.

Interestingly, the C/S cathodes deliver gradually elevated coulombic efficiencies with increasing Al₂O₃ coating cycles. Especially, the electrodes with 10-cycle and 20-cycle Al₂O₃ coating display coulombic efficiencies over 90 %, in comparison with 70 % of bare C/S composite. The improved coulombic efficiency indicates that Al₂O₃ coating can relieve the “shuttle effect”. FE-SEM images of electrodes after 30 discharge-charge cycles further reveal the protection of polysulfides by Al₂O₃ coating. The Al₂O₃ coated electrodes show fewer discharge products deposited onto the surface (Fig. 3b, 3c), while the bare C/S electrode is almost totally covered by bulk of discharge products (Fig. 3a). Based on aforementioned discussion, Al₂O₃ coating is responsible for the restrained polysulfide dissolution and the suppression of insulated discharge product deposition. With ultrathin coating (2-cycle Al₂O₃), sulfur cathode performs much better cycling capacities and stability. Thicker ALD coating (10-cycle, 20-cycle Al₂O₃) delivers higher stability but reduced cycling capacities for sulfur cathodes. It should be mentioned that although Al₂O₃ coating can relieve the dissolution of polysulfide, it still cannot totally eliminate the
“shuttle effect” since $\text{Al}_2\text{O}_3$ is a brittle material with limited durability. Synchrotron-based XPS was carried out in order to elucidate the reason for the improved performance with ultrathin $\text{Al}_2\text{O}_3$ coating.

![Image](image.png)

**Figure 6.5** Proposed schematic of $\text{Al}_2\text{O}_3$ coating effects on sulfur cathodes with (a) blank, (b) ultrathin, and (c) relatively thick $\text{Al}_2\text{O}_3$ coating.

Al 2p XPS spectra are shown in **Figure 6.4a**. The intensities of Al 2p peaks are gradually strengthened from 2-cycle to 10-cycle $\text{Al}_2\text{O}_3$ coating, demonstrating a thicker coating layer formation with increasing ALD cycles. Moreover, Al 2p peaks of electrodes with increasing $\text{Al}_2\text{O}_3$ layers are distributed from high to low binding energy after battery test. Two major Al 2p peaks display in all of the spectra, as shown in **Figure 6.4b**, one at 75.5 eV assigned to $\text{Al}_2\text{O}_3$, and the other at 77.5 eV to $\text{AlF}_3$ [32]. Al 2p peaks of 2-cycle $\text{Al}_2\text{O}_3$ electrode, except for $\text{AlF}_3$ and $\text{Al}_2\text{O}_3$, another weak peak at about 72.2 eV is also observed which can be assigned to $\text{LiAlO}_2$ [32, 33]. It has been reported by Xiao’s group that the formation of $\text{AlF}_3$ and $\text{LiAlO}_2$ is favorable to the ionic conductivity of cells, which reduces the energy barriers of Li-ion diffusion [32]. Thus, in our case, an artificial ionic conductive
SEI layer is formed from the Al₂O₃ coating after lithiation/delithiation processes. The ionic conductive SEI layer is not only a protection of polysulfide, but also a support for Li-ion diffusion, resulting in high utilization and reversibility of sulfur cathode (shown in Figure 6.5b) [29]. Al 2p spectrum of 10-cycle Al₂O₃ electrode also shows two peaks of AlF₃ and Al₂O₃. However, it exhibits a strong peak of Al₂O₃ and a weak one of AlF₃, suggesting that the formation of AlF₃ and LiAlO₂ only occurred on the top layer of ALD coating. Despite the effective protection on polysulfides, thicker Al₂O₃ coating reduces the utilization of sulfur due to the insulating coating layer, resulting in a high cycling stability with lower capacities (shown in Figure 6.5c).

6.4 Conclusion

In this paper, we studied a series of ALD Al₂O₃ coating on the performance of carbon-sulfur electrodes. The 2-cycle ALD Al₂O₃ electrode showed an impressive cycling capacity compared with bare C/S electrode, of which the discharge capacity maintained 630 mAh g⁻¹ after 70 cycles. 10-cycle and 20-cycle ALD Al₂O₃ electrodes achieved coulombic efficiency over 90 %, demonstrating a significant improvement of battery cycling stability. Confirmed by synchrotron-based XPS result, AlF₃/LiAlO₂ layer was formed during lithiation/delithiation processes which served as an ionic conductive layer to improve the utilization of sulfur active material. Thereby, ALD Al₂O₃ coating performs as an SEI layer to preserve polysulfides migration and suppress the deposition of insulating discharge product on electrodes, improving both the stability and capacities of Li-S batteries. This work elucidates ALD Al₂O₃ coating effects on sulfur cathodes and will inspire advanced ALD applications on Li-sulfur batteries.

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References


Supporting information

Figure S6. TGA curves of pristine carbon-sulfur composites, 2-cycle Al₂O₃ C/S composites, and 20-cycle Al₂O₃ C/S composites.
Figure S6. 2 FE-SEM and Al elemental mapping images of C/S electrode with 5-cycle (a, b, c), 10-cycle (d, e, f), and 20-cycle (g, h, i) ALD Al$_2$O$_3$ coating.

Figure S6. 3 FE-SEM image of pristine carbon-sulfur electrode.
Figure S6.4 Comparison of Al 2p peaks of AlF$_3$ with different ALD cycles.
Chapter 7

7 Superior stable sulfur cathodes of Li-S batteries enabled by molecular layer deposition

As reported reference, the structure and component of coating materials directly affects the electrochemical performance of Li-S batteries. ALD has been reported as coating material for sulfur cathodes with ultrathin thickness and uniform deposition. However, it should be noted that the conductivity of Al$_2$O$_3$ is limited, and dense structure of coating layer from metal oxide may be not benefit for electrolyte penetration.

Molecular layer deposition is one novel thin film technique. Close to ALD, this thin film technique also undergoes self-limited reaction and enables to control the thickness of thin film precisely. On contrary, MLD thin film introduces carbon contained organic molecule as precursor and therefore facilitates the growth of metal-organic hybrid thin film. The introduction of carbon contained precursor provides the potential to fabricate high conductive thin film, and the long-chain unit of organic precursor in MLD thin film enables to form porous structure thin film. Besides, it has been demonstrated MLD metal-organic hybrid thin film has improved mechanical properties to accommodate the volume expansion of sulfur cathodes. Thereby, MLD thin film as coating material may bring significant improvement for sulfur cathode.

In this chapter, MLD alucone is applied as coating material for sulfur cathodes. Detailed coating effect is investigated via different physical and electrochemical characterizations. The study also makes a comparison of MLD alucone coating and ALD Al$_2$O$_3$ coating for sulfur cathodes. It has been demonstrated that MLD alucone coating presents improved electrochemical performance with stabilized and prolonged cycle life for sulfur cathodes, which is a promising coating material for Li-S batteries in practical.

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7.1 Introduction

Li-sulfur batteries have been intensively studied in recent years owing to their high theoretical capacity and energy density, and are being considered as the most promising power candidate for electric vehicles and hybrid electrical vehicles [1, 2]. However, the reality of commercial Li-S batteries is hindered by its poor cycle life [3]. One critical issue currently in Li-S batteries is the well-known “shuttle effect”, which is caused by the dissolution of polysulfide. The polysulfide species migrate to the anode and chemically react with Li metal, resulting in Li metal corrosion as well as irreversible sulfur loss [4]. Furthermore, the insulating nature of sulfur and its large volume expansion during the lithiation process hinder the commercialization of Li-S batteries [5, 6].

Surface coating with carbon or metal oxides has been proven a promising approach towards mitigating the “shuttle effect” in Li-S batteries [7-10]. In previous studies, surface coatings were generally conducted on sulfur composite by solution-based methods. Unfortunately, it is hard to reach good control over the uniformity and thickness of the coating layer, which are essential to achieve the optimal performance of sulfur composite in Li-S batteries. Ideally, the surface coating on sulfur cathodes should be mechanically robust to accommodate the large volume expansion, as well as be thin enough to effectively prevent the dissolution of polysulfide without blocking ion and electron transport [11-13]. Atomic layer deposition (ALD) is an ideal technique to synthesize ultrathin and conformal coatings due to the self-limiting nature [14, 15]. Al2O3 coating via ALD has been studied for sulfur cathodes [16, 17]. The ultrathin, conformal metal oxide coating layer prevents the migration of polysulfides to improve the stability of Li-S cells [16, 17].

Molecular layer deposition (MLD), an analogue of ALD, also provides precise control over film thickness and allows for conformal film growth over nanostructure substrates [18-20]. However, ALD is limited to metal oxides or metal films, whereas MLD can be employed to produce pure polymeric thin films or inorganic-organic hybrid thin films [21]. The combination of ALD and MLD to produce inorganic-organic hybrid thin films holds many advantages such as lower growth temperatures, tunable thermal stability, and improved mechanical properties [22-25].
Furthermore, the toughness and flexibility of polymeric metal thin films by MLD is strengthened with the introduction of C-C and C-O bonds in this system [18, 19, 26]. Lee et al. [27] reported a flexible MLD coating employed on Si anode to accommodate its huge volume expansion, and significantly improve cycling stability of Si anode.

Herein, for the first time, we demonstrate that an MLD alucone coating directly on sulfur electrodes can dramatically improve the cycling stability and capability of Li-S cells. Furthermore, the alucone coated sulfur cathode delivers a discharge capacity of 710 mAh g\(^{-1}\), which is over two times higher than the bare sulfur cathode after 100 cycles. The improvement in the electrochemical performance could be attributed to the mitigation of “shuttle effect” by alucone coating.

### 7.2 Experimental

#### 7.2.1 Preparation of carbon-sulfur electrode

Commercial carbon black was mixed with sulfur powder and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained sulfur-carbon black composites maintained 65 wt% sulfur loading. The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 70:20:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum.

#### 7.2.2 Preparation of alucone coating on C/S electrode by MLD

Molecular layer deposition of alucone was conducted in a Gemstar-8 ALD system (Arradiance, USA). Alucone was directly deposited on the C/S electrode at 100 °C by alternatively introducing trimethylaluminium (TMA) and Ethylene Glycol (EG). The sulfur loading of the C/S electrode dropped by 5 wt% after alucone coating.

#### 7.2.3 Physical and electrochemical characterization

The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV. CR-2032 type coin cells were
assembled in an argon-filled glove box. The coin-type cells consisted of Li metal as the anode, Celgard 2400 as separator, and the C/S electrode prepared above as the cathode. The electrolyte was composed of 1M LiTFSI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under a scanning rate of 0.1 mV s\(^{-1}\) between 1.0 V - 3.0 V (vs. Li/Li\(^+\)). Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V - 3.0 V (vs. Li/Li\(^+\)) at room temperature using an Arbin BT-2000 Battery Test equipment. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min on the SDT Q600 (TA Instruments).

### 7.3 Results and Discussion

Alucone film was directly deposited on as-prepared sulfur-carbon electrodes (C/S electrodes) using trimethyl aluminium (TMA) and ethylene glycol (EG) as precursors at 100 °C. MLD of alucone from TMA and EG has been well studied, and can be performed at low temperatures [18, 22]. Direct coating on the electrode at this low temperature retains the electron-conductive network [14] and avoids the evaporation of sulfur (ESI†). Figure 7.1 illustrates the surface reactions between TMA and EG occurring in one typical MLD cycle, and alucone thin film is coated on the sulfur cathode by repeating the MLD cycles. The influence of alucone coating thickness is investigated in detail with 2, 5, 10 and 20 MLD cycles being deposited on sulfur electrodes.

Figure 7.1 Schematic of alucone MLD thin film formation as coating layer applied on C/S cathode. The self-limiting reaction is conducted by using two precursors to produce a layer-by-layer inorganic-organic hybrid composite
Figure 7.2 (a) Cycle performance of bare, 2-, 5-, 10-cycle alucone coated C/S cathodes under 160 mA g\(^{-1}\); (b) typical discharge-charge profiles of sulfur cathodes with/without alucone coating; (c) comparison of rate performance between 5-cycle alucone coated and bare C/S electrodes.

Electrochemical characterization was carried out to evaluate the effect of the alucone coating on the performance of sulfur cathodes. Figure 7.2a shows the cycling performance of sulfur cathodes with/without alucone coating measured at a current density of 160 mA g\(^{-1}\). All of the alucone coated sulfur cathodes perform significant improvement in both cycling capability and columbic efficiency (CE). Interestingly, the 5-cycle alucone coated sulfur cathode delivers a specific discharge capacity of 710 mAh g\(^{-1}\) after 100 cycles, which is over two times greater than that of bare C/S cathode (310 mAh g\(^{-1}\) of 100 cycle). Furthermore, alucone coated C/S cathodes retain a stable CE over 90 %, as opposed to only 70-80 % of the bare C/S cathode. The impressive cycling stability of alucone coated sulfur cathode elucidates that the strengthened coating layer effectively protects polysulfides...
from migration, resulting in prolonged durability of Li-S batteries. 10-cycle alucone coated sulfur cathode also demonstrates improved cycling stability and maintains a capacity over 80 % from the 25th to 100th cycle. However, the 10-cycle alucone coated cathode delivers a lower initial specific discharge capacity of 1155 mAh g\(^{-1}\), which could be due to the limited sulfur utilization as a result from the thick alucone coating [27]. The 2-cycle alucone coated sulfur cathode delivers progressive degradation with cycling, indicating that 2-cycle alucone coating is too thin to protect C/S cathode effectively.

To reveal the detailed electrochemical processes occurring within each system, discharge-charge profiles of sulfur cathodes are shown in Figure 7.2b. The bare and 5-cycle alucone coated cathodes demonstrate typical Li-S redox process, which performs two potential plateaus at 2.3 V and 2.1 V during discharge process, and one potential plateau at about 2.4 V during charge process. The bare C/S cathode shows an obvious overcharge effect due to the serious “shuttle effect”, accounting for the low CE in cycling performance [28-30]. The 5-cycle alucone coated cathode presents a nearly closed circle in its discharge-charge profile, indicating effective alleviation of the “shuttle effect” by the alucone coating [6]. Furthermore, the sulfur cathode with 5-cycles of alucone coating shows flat potential plateaus, which are an indication of high reversibility of Li-S redox reaction. On the other hand, the 10- and 20-cycle alucone coated cathodes show extreme potential polarization, suggesting limited conductivity and low reaction activity of sulfur cathodes with thicker alucone coatings (Figure S7.4, S7.5).

Figure 7.2c demonstrates the rate performance of 5-cycle alucone treated cathode against bare C/S cathode. The electrodes are tested at 160 mA g\(^{-1}\) for the first 2 cycles and then subsequently increased to 6400 mA g\(^{-1}\) during cycling. The 5-cycle alucone coated sulfur cathode demonstrates a discharge capacity of 700 mAh g\(^{-1}\) under 6400 mA g\(^{-1}\), and returns to 750 mAh g\(^{-1}\) after 80 cycles. The improved rate performance confirms that the ultrathin layer of alucone not only relieve the “shuttle effect” from dissolved polysulfide but also allow lithium-ion fast diffusion under elevated test conditions [13].
The morphology of electrodes with/without alucone coating was examined before and after battery cycling, in order to reveal the improved performance by alucone coating. As seen in Figure 7.3, the morphology of the sulfur cathode with/without alucone coatings show agglomeration of nanoparticles within sizes of 40-60 nm (Figure 7.3a, 7.3c). After cycling, the bare C/S electrode is completely covered with discharge products due to the polysulfide dissolution (Figure 7.3b), which is accountable for the reduced sulfur reversibility and elevated shuttle effect during cycling (Figure 7.2) [7, 31, 32]. Different from the bare C/S cathode, the alucone coated C/S cathode displays a limited amount of discharge products being deposited on the surface after cycling (Figure 7.3d), suggesting that the dissolved polysulfides are restrained in the carbon matrix by alucone coating (Figure S7.8, S7.9). The reduced dissolution of polysulfides by alucone coating leads to the greatly improved cycling stability and CE for C/S cathode. Moreover, it is believed that the good mechanical properties of the alucone coating should contribute to the accommodation of volume expansion in sulfur cathode during cycling [19, 23, 27], thus extent the durability for sulfur cathodes. In addition, the stable performance of the alucone coated C/S cathode is also attributed to the retained conductive network in the electrode after coating.
Figure 7.4 Cycle performances of bare, ALD-Al2O3 coated, and MLD-alucone coated C/S cathodes at a current density of 160 mA g\(^{-1}\).

Previous studies have shown that ALD-Al2O3 coating could enhance the performance of C/S cathodes. In this work, we found that the performance of C/S cathode with alucone coating by MLD is even better than the optimized ALD- Al2O3 coated C/S cathode. Figure 7.4 compares on the performance of MLD-alucone coated, ALD-Al2O3 coated, and bare C/S cathodes. Among these samples, it is obvious that the MLD-alucone coated C/S cathode demonstrates the most promising result with enhanced stability and prolonged lifespan, which delivers a capacity of 620 mAh g\(^{-1}\) after 150 cycles (Figure S7.7).

7.4 Conclusion

In summary, for the first time, inorganic-organic hybrid alucone coatings via MLD have been investigated on sulfur cathodes. The alucone coating layer provided not only solid protection of sulfur from dissolution, but also an ultrathin layer to allow fast Li-ion diffusion, resulting in improved cycling stability of Li-S cells. 5-cycle alucone coated sulfur cathode delivered a discharge capacity of 710 mAh g\(^{-1}\) in 100 cycles under 160 mA g\(^{-1}\), and about 700 mAh g\(^{-1}\) under 6400 mA g\(^{-1}\) over 50 cycles. The alucone coating demonstrated long durability during cell cycling, which explores a new direction in the protection of sulfur cathode. Although the alucone film has limited conductivity, the introduction of carbon element in the MLD process holds the possibility building an ideal conductive, long durable, as well as ultrathin conformal coating layer for sulfur cathode in our future endeavors.
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References


Supporting information

**Figure S7.1** Schematic of atomic layer deposition Al$_2$O$_3$ coating on carbon-sulfur cathode. A typical Al$_2$O$_3$ ALD chemical reaction is conducted using H$_2$O and TMA as precursors.

**Figure S7.2** FE-SEM and Al elemental mapping of 5-cycle alucone coated C/S electrode. The EDX result confirms alucone coating uniformly growing on electrode under micrometer magnification.
Figure S7. 3 TGA curves of carbon-sulfur composite with/without alucone coating.
Figure S7. 4 (a) Cycle performance under 160 mA g$^{-1}$ and (b) discharge-charge profiles of 5-, 10-, and 20-cycle alucone coated C/S electrode. The 20-cycle alucone coated cathode showed lower initial discharge capacity and serious potential polarization, confirming the thick coating layer hinder the transmission of Li-ions.
Figure S7. 5 EIS spectra of sulfur cathodes with and without alucone coating.

(a) Before cells test, the three cells all show very small surface electron transfer resistances, confirming the alucone coating retain the conductivity of electrode. (b) After over 30-cycle discharge-charge process, the alucone coated cathodes still maintain small surface electron transfer resistances, whereas the bare C/S cathode shows a big half circle, corresponding to the low conductivity of electrode resulting from deposited discharge product on surface (shown in Figure 7.3b). Furthermore, it should note that the 10-cycle alucone coated electrode shows a short line between the half circle and straight line in the two spectra (brown circle). The short line can be considered as a semi-infinite diffusion derived from thick 10-cycle insulating coating layer, corresponding to reduced conductivity of thick 10-cycle alucone coated cathode.
Figure S7. 6 Cycle performance of 5-cycle alucone coated cathode under different current densities. The coated cathode can retain over 600 mAh g\(^{-1}\) under 1600 mA g\(^{-1}\) over 100 cycles.
Figure S7. Cycle performances of bare, ALD-Al₂O₃ coated, and MLD-alucone coated C/S cathodes at a current density of 160 mA g⁻¹.

It should be noted that the conductivity of alucone coating layer is limited, and may cause the drop of capacity during cycling. Compared with ALD Al₂O₃ coating, it is demonstrated that the hybrid inorganic-organic MLD alucone layer improves thermal stability and flexibility. Lee et al reported a similar flexible Al-GC coating to accommodate the huge volume expansion of Si to achieve the high reversibility of Si anode (Adv Mater, 2014, 26, 1596.). Theses advanced properties of MLD coating are proposed to improve the performance of sulfur cathodes better than that of ALD coating in long cycle life.
Figure S7.8 A proposed mechanism of alucone coating effect during lithiated process.

The bare C/S electrode after cycling is covered by discharge product (Fig. S8b), which is due to the polysulfides dissolution and finally formed insulated discharge product covered on surface, as shown in Fig. S8c. On the other hand, the alucone coated electrode after cycling shows an increased particle size, which can be proposed that the dissolved polysulfides are trapped by alucone coating, as shown in Fig.S8f.
The alucone coated electrodes obviously show fewer discharge product depositing on surface, which confirms the coating layer prevent the dissolution of polysulfides. Interestingly, the particle size of electrodes is increased with the increasing MLD coating cycles. This may due to the particle with thicker coating layer show more obvious expansion than that of the particle with thin coating layer during the lithiation process. The mechanism of expanded particle with alucone coating is proposed that alucone coating layer is flexible to accommodate the volume expansion of sulfur cathode during cycling, which improve the performance of sulfur cathode in long cycle life (*Adv Mater*, 2014, **26**, 1596). Further study with detailed MLD coating effect and other MLD coating materials will be underwent in our future work.
Chapter 8

8 Safe and durable high-temperature lithium-sulfur batteries via molecular layer deposited coating

Most study of Li-S batteries is based on the use of ether based electrolyte in this system. However, it should be noted that ether based solvents have very low boiling and flash point, which is not a safe choice for Li-S batteries. Especially of Li-S batteries applied for electric vehicles (EVs), the cells with ether based electrolyte will bring safety hazard operated under high temperature. Carbonate based electrolyte has safe and stable properties for high-temperature Li-ion batteries. However, the side-reaction between sulfur species and carbonate solvents results in a failure of Li-S batteries. Therefore, to address safe high temperature Li-S batteries, it should design a reversible sulfur electrode operating in carbonate electrolyte.

MLD alucone coating has been demonstrated significant improvement of electrochemical performance for Li-S batteries. The ultrathin coating layer protects sulfur electrodes from dissolution and still allows the smooth transportation of Li-ions. Based on aforementioned properties, MLD alucone coating in this chapter is applied as coating for sulfur electrode in carbonate based electrolyte. As demonstrated from electrochemical performance, the coating layer effectively protects sulfur from side-reactions with carbonate based solvents and completes a solid-phase electrochemical reaction of Li-S battery. The MLD alucone coated electrode presents an ultra-stable and prolonged cycle life under high temperature, and detailed mechanism of this coating material with electrochemical process are carried out via synchrotron based X-ray study.

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8.1 Introduction

Lithium-sulfur battery is an attractive energy storage system due to the ultrahigh theoretical energy density compared to Li-ion batteries, and therefore considered as a promising energy device to meet the growing energy demands for high power output applications such as electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1, 2]. From a practical and industrial perspective, a critical requirement of batteries in EVs and HEVs is safe operation with a wide temperature window [3, 4]. Unfortunately, state-of-art ether based electrolytes for Li-S batteries suffer from low boiling and flash points (Table S8.1), and therefore pose significant safety risks for operation at elevated temperatures. In addition, the commonly used LiNO₃ additive is an oxidizing agent and provides further safety concerns [5, 6]. Moreover, high temperatures also promote lithium polysulfide dissolution into the electrolyte, resulting in poor cycle life [7, 8]. These safety concerns have considerably restricted the potential application of Li-S batteries in EVs with the use of ether based electrolyte and may involve the re-designation of sulfur cathodes in practical [9-12].

One possible solution in addressing these temperature issues for Li-S batteries is re-visiting the use of traditional carbonate based Li-ion electrolytes, which have been developed and adopted for lithium-ion batteries (LIBs) over three decades [13-15]. Unfortunately, attempts in employing carbonate based electrolytes for Li-S batteries were rarely succeeded due to side reactions between carbonate solvents and electrochemical intermediates such as lithium polysulfide species, resulting in the irreversible electrochemical behavior of batteries [13-15]. Very recently, a possible approach has been developed to solve this issue by capturing sulfur within fine holes tailored into carbon hosts [16, 17]. The confined sulfur molecules undergo solid-state electrochemical conversion to avoid solution based side reactions. However, it still needs specially manufactured microporous carbon-sulfur composites, which requires delicate control in laboratory-scale fabrication. Thereby, a critical question now arises: Is there a simple and versatile approach to be used in sulfur cathodes with carbonate based electrolytes to realize the safe operation of Li-S batteries at high temperature?
Atomic layer deposition (ALD) and molecular layer deposition (MLD) have gained considerable attention as ideal ultrathin-film techniques for the applications in energy storage systems [18-21]. With self-limiting binary reactions, MLD demonstrates unparalleled advantages in producing uniform and conformal thin films, providing precise and flexible control over film thickness and chemical composition of the target material at a molecular scale [20, 21]. Furthermore, the introduction of organic precursors during the deposition process enables the synthesis of hybrid metal-polymeric thin films. Up to now, ALD and MLD have been used to produce protective coating materials, solid-state electrolytes, and electrode materials for Li-based batteries to improve their cycle life and safety [21-23].

In this report, we propose a novel strategy to enable the use of carbonate-based electrolyte with universal carbon-sulfur electrodes of secondary Li-S batteries by MLD. Instead of elaborately designed microporous carbon, commercially available mesoporous carbon is employed as a sulfur host to demonstrate the universal application of MLD. The MLD alucone thin film material we employed in this research has demonstrated desirable flexible mechanical properties as a coating material for Li-ion and Li-S batteries, exhibiting solid and prolonged protection for electrodes during cycling [23, 24]. Furthermore, a number of excellent papers have demonstrated the use of ALD Al₂O₃ coating for sulfur cathodes, demonstrating improved cycle performance as well as stabilized and prolonged cycle life for Li-S batteries [25, 26]. The MLD alucone film in this report acts as an effective protecting layer and enables a reversible charge/discharge behavior for carbon-sulfur electrodes in carbonate-based electrolytes by preventing side reactions from occurring between sulfide/polysulfide intermediates and carbonate solvents. With the MLD coated carbon-sulfur electrodes, we demonstrate that high temperature Li-S batteries have safe and stable ultra-long cycle life operating in carbonate-based electrolyte. Furthermore, synchrotron-based measurements were carried out to reveal the underlying mechanism of MLD coating in Li-S batteries.

8.2 Experimental

Preparation of carbon-sulfur electrode: Commercial carbon black (KJ EC-600, US) was mixed with sulfur powder (99.5 %, Sigma-Aldrich) and dried at 80 °C for 12 h to remove
moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained carbon-sulfur composites (C-S) maintained 65 wt% sulfur loading. The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 70:20:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum.

Preparation of alucone coating on C-S electrode by MLD: Molecular layer deposition of alucone was conducted in a Gemstar-8 ALD system (Arradiance, USA). Alucone was directly deposited on the C-S electrode at 100 °C by alternatively introducing trimethylaluminium (TMA) and Ethylene Glycol (EG). As studied from previous research, the growth rate of alucone thin film is < 0.3 nm/MLD cycle, and the sulfur loading of the C-S electrode dropped by 5 wt% after alucone coating.

Electrochemical characterization: CR-2032 type coin cells were assembled in an argon-filled glove box. The coin-type cells consisted of Li foil as the anode, polypropylene membrane (Celgard 2400) as separator, and the C-S electrode prepared above as the cathode. Two electrolyte systems were selected in this research: (1) carbonate-based electrolyte composed of 1 M LiPF₆ solution in ethylene carbonate:diethyl carbonate:ethyl methyl carbonate (EC:DEC:EMC) with a volume ratio of 1:1:1, and (2) ether-based electrolyte composed of 1 M LiTFSI salt in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under a scanning rate of 0.1 mV s⁻¹ between 1.0 V - 3.0 V (vs. Li/Li⁺). Electrochemical impedance spectroscopy (EIS) was also performed on the versatile multichannel potentiostat 3/Z (VMP3) by applying an AC voltage of 5 mV amplitude in the 100 kHz to 100 mHz frequency range. All of batteries were tested by holding 6 hours after assembling. Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V - 3.0 V (vs. Li/Li⁺) at room temperature using an Arbin BT-2000 Battery Test equipment.

Physical characterization: The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) equipped with energy
dispersive spectroscopy (EDS). Fourier transform-infrared (FTIR) measurements were determined by KBr method with a Nicolet 6700 FT-IR recorded in the transmittance mode over range of 400-4000 cm$^{-1}$ spectra by averaging 40 scans with a resolution of 8 cm$^{-1}$. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min on the SDT Q600 (TA Instruments). Syntrochron based near edge X-ray absorption fine structure (NEXAFS) and high energy X-ray photoelectron spectra (HEXPS) measurements were carried out under two separate beamlines. Sulfur K-edge X-ray NEXAFS spectra were collected in total electron yield (TEY) mode on beamline 10.3.2 in the Advanced Light Source at Lawrence Berkeley National Laboratory. Sulfur 1s HEXPS spectra was conducted on the Soft X-ray Microcharacterization beamline (SXRBM) with different values of photo energy at the Canadian Light Source (CLS) at the University of Saskatchewan in Saskatoon. Before synchrotron radiation experiments, original C-S electrodes and after battery test ones were prepared under protected environment. To avoid oxidation of samples, the C-S electrodes after discharge-charge processes were obtained from coin cells and sealed in glovebox under Argon, and then transferred to the corresponding beamlines for further measurements.

8.3 Results and Discussion

As shown in Figure 8.1, MLD process employs subsequent exposures of trimethylaluminum (TMA) and ethylene glycol (EG) into the reaction chamber to form a thin metal-organic coating on C-S electrodes. This reaction occurs in two half-reactions to form one monolayer of alucone (an inorganic-organic thin film composed of Al$_2$O$_3$ unit linked by –O-C$_2$H$_4$-O- units), as shown in Figure 8.1. The thickness of the alucone coating can be precisely controlled by the number MLD cycles applied. In Figure 8.2a, SEM image demonstrates that the diameter of C-S particles in a 10-cycle alucone coated electrode ranges between 40-60 nm, which is close to that of the pristine C-S electrodes (Figure S8.3 and Figure S8.6). Elemental mapping using energy dispersive spectroscopy (EDS) reveals that the alucone coating is uniform along the surface of the film. Furthermore, cross sectional EDS analysis confirms that the MLD alucone film is also evenly distributed throughout the electrode vertically, demonstrating the conformal and uniform nature of the
MLD process. Synchrotron based high energy X-ray photoelectron spectroscopy (HEXPS) further elucidates the interaction between sulfur and alucone coating. As shown in Figure 8.3f, compared to pristine C-S electrodes, the sulfur 1s spectrum for alucone coated electrode displays an additional peak at 2475.0 eV, demonstrating that part of sulfur was oxidized during the MLD process and via S-O interaction with alucone coating. Sulfur 1s spectra with different photo energies and FTIR spectra were also conducted to further understand the interaction between alucone coating and sulfur, as shown in Figure S8.7 and Figure S8.8.

**Figure 8.1** Schematic diagram of alucone coating on C-S electrode via molecular layer deposition.
Figure 8.2 (a-b) FE-SEM images of alucone coated C-S electrode. (c-d) EDS elemental mapping profiles of (b). (e) Linear-scanning EDS analysis of cross-section of alucone coated C-S electrode on silicon substrate. (f) Sulfur 1s HEXPS spectra of alucone coated and pristine C-S electrodes.

Electrochemical behavior of alucone coated and pristine C-S electrodes were evaluated using carbonate-based electrolyte (1M LiPF$_6$ in ethylene carbonate (EC): ethyl-methyl carbonate (EMC): diethyl carbonate (DEC) solvents with 1:1:1 of volume ratio). Figure 8.3a displays the cycle performance of C-S electrodes under 0.1 C at room temperature (RT). Interestingly, alucone coated C-S electrodes exhibit dramatically improved performance in carbonate-based electrolyte compared to pristine electrodes. The alucone coated electrode shows an initial capacity of 912 mAh g$^{-1}$ and stabilizes at 429 mAh g$^{-1}$ after 100 cycles. In contrast, the pristine C-S electrode shows an initial discharge capacity of 940 mAh g$^{-1}$, however, by the second cycle the discharge capacity significantly drops to 159 mAh g$^{-1}$, indicating irreversible electrochemical processes occurred, which is consistent with previous studies [6, 15]. Discharge-charge curves (Figure 8.3b) and corresponding cyclic voltammograms (CVs) (Figure 8.3c and Figure 8.3d) provide further
evidence that drastically different electrochemical processes had taken place in the coated and uncoated electrodes. In a typical Li-S battery where ether-based electrolyte is employed, two cathodic peaks at 2.3 V and 2.1 V appear during the lithiated sulfur reaction, corresponding to the reduction of the S₈ molecule to long chain polysulfides and then short chain sulfides in a two-step reaction; the anodic peak at 2.4 V corresponding to a reversed process, as shown in Figure S8.10 [27-29]. Interestingly, the pristine C-S electrode cycled in carbonate-based electrolytes displays a single broad cathodic peak at 2.5 V in the first cycle and no peaks appeared in subsequent cycles. This type of behavior is indicative of long-chain polysulfides formation which may inhibit further electrochemical reaction [15]. However, the alucone coated C-S electrode exhibits well-defined potential plateaus during the discharge and charge process, as well as reproducible cathodic and anodic peaks in the CV profile. Compared to typical Li-S redox reactions, alucone coated electrodes display a larger voltage gap between the cathodic and anodic peaks (1.5 V and 2.5 V), representing an alternative reaction route as well as increased internal resistance [30, 31]. Electrochemical impedance spectra (EIS) were conducted to understand the influence of the MLD alucone coating layer on the conductivity of the electrode, as shown in Figure S8.12. The results indicate that the alucone coating layer maintains high activity toward electrochemical reactions for electrodes cycled in various electrolytes.
Figure 8.3 (a) Electrochemical cycle performance and (b) discharge-charge profiles of coated and pristine C-S electrode. Cyclic voltammetric profile of (c) pristine C-S electrode and (d) coated C-S electrode. (e) Comparison of alucone coated C-S electrodes running within carbonate based and ether based electrolyte under 55 °C. (f) Discharge-charge profiles of alucone coated electrode operating in carbonate based electrolyte under 55 °C.

To demonstrate the electrochemical performance of the Li-S batteries at high temperature, the cycle stability of alucone coated C-S electrodes with both carbonate- and ether-based electrolytes were measured at 55 °C to simulate the environment for Li-S batteries in electric vehicles (Figure 8.3e). Impressively, alucone coated C-S demonstrates improved capacity and extended cycle life in Li-S batteries using carbonate-based electrolyte. Alucone coated electrodes exhibits an initial capacity of 1055 mAh g⁻¹, a value that exceeds the initial capacity conducted at room temperature. Elevated temperatures facilitate the diffusion of Li-ions and promote electrochemical reactions, resulting in improved battery performance [32, 33]. The capacity of the cell stabilizes at 661 mAh g⁻¹ after 50 cycles and with a capacity retention over 573 mAh g⁻¹ after 300 cycles, demonstrating extraordinary
cycle life. Cyclic discharge-charge curves further demonstrate that the electrochemical processes taking place in alucone coated C-S electrodes operating at 55 °C is highly reversible. As shown in Figure 8.3f, potential plateaus in discharge and charge curves are stabilized at 2.0 V and 2.3 V, displaying improved electrochemical activity at elevated temperature. For comparison, alucone coated C-S electrode was also cycled at 55 °C with ether-based electrolyte (1M LiTFSI in dimethoxyethane (DME): dioxolane (DOL) with 1:1 of volume ratio), as outlined in Figure 8.3e, which shows a rapid capacity decay with cell failure after 100 cycles. As mentioned earlier, the flash point of ether solvents DME and DOL is below 2 °C, which raises a number of safety issues for high temperature operation of Li-S batteries. Although 55 °C does not reach to boiling temperature of ether based electrolytes, this elevated temperature can still result in higher vapor pressure while also enhancing electrolyte consumption, bringing a number of deleterious effects into question [9-12]. Based on these results, MLD alucone coating enables the use of secondary C-S cathodes in carbonate-based electrolyte, and offers a safe and versatile approach toward Li-S batteries at elevated temperature.

Figure 8.4 Sulfur K-edge spectra of C-S electrodes at discharge-charge steps. (a) Pristine C-S with carbonate based electrolyte; (b) alucone coated C-S with carbonate based electrolyte; and (c) pristine C-S with ether based electrolyte.

Near edge X-ray absorption fine structure (NEXAFS) was conducted to further elucidate the mechanism behind the MLD alucone coating in C-S electrodes cycled in carbonate electrolyte. Figure 8.4 displays the S K-edge spectra for pristine C-S and alucone coated
electrodes under discharge-charge steps to explore the chemical structure evolution of different electrodes. According to previous studies, the feature at 2472.2 eV can be attributed the S 1s transition to S–S π* state of elemental sulfur. Features located at 2476.2, 2478.0, 2480.5, and 2482.3 eV are assigned to the S 1s transition to Li2S σ*, S2– σ* and/or SO32– σ*, COSO2– σ*, and SO42– σ*, respectively. As shown in Figure 8.4a, pristine C-S electrodes during discharge-charge processes do not exhibit obvious peak shifts, and only presents one new peak at 2474.0 eV. This additional peak most likely arises from side reactions occurring between long-chain polysulfides and carbonate-based solvents, producing Sx-Cn-C=O- species [15, 37, 38]. It has been reported that this side reaction results in solvent decomposition which in turn hinders lithium ion diffusion [15]. This observation, combined with the CV results, allows us to propose with confidence that the failure in uncoated C-S electrode in Li-S batteries with carbonate-based electrolytes can almost certainly be attributed to the reaction of long chain polysulfides with carbonate solvents. On the other hand, as shown in Figure 8.4b, the S K-edge spectra for alucone coated C-S electrodes show an interesting phenomenon. Prior to electrochemical testing, the NEXAFS spectra of the coated electrodes show an additional peak at 2473.6 eV assigned to C-S chemical bond, which indicates a chemical interaction between sulfur and alucone coating [39]. During the discharge-charge process, the S-S peak from alucone coated C-S electrode initially shifts from 2472.2 to 2473.4 eV, then returns to 2472.2 eV. This evolution is drastically different from the behavior of pristine C-S electrodes and is indicative of a reversible Li-S redox reaction occurring with the use of alucone coating [39, 40]. Previous literature results indicates that a shift in the S-S peak can be attributed to the transformation of elemental sulfur to polysulfides species, indicating an interaction between polysulfides and alucone coating layer [39, 40, 41]. The final discharge product of the alucone coated C-S electrode (discharge 1.0 V) can be determined as Li2S, as shown in Figure S8.15 [41, 42]. XANE spectra of polysulfides S_n^{2–} exhibit a pre-edge peak at around 2470.2 eV along with a peak at 2472 eV. The Li2S reference sample, on the other hand, only exhibits two peaks at 2470.8 and 2473.7 eV without any indication of a pre-edge peak. Compared to the reference sample, the spectra of alucone coated C-S electrode discharged to 1.0 V is in agreement with Li2S, suggesting that sulfur can be reduced to Li2S as the final discharge product in carbonate based electrolyte. Further, few SO4^{2–} species are
identified throughout the electrochemical process, which is still an open question and most like arises from the oxidation of sulfide species by alucone coating. From the comparison of Figure 8.4a with 8.4b, it is apparent that the major drawback for pristine C-S electrodes cycled in carbonate-based electrolytes is the occurrence of side reactions between long chain polysulfides and the surrounding carbonate solvents. From the S K-edge NEXAFS and the S 1s HEXPS spectra shown in Figure 8.2f, we propose that the alucone coating interacts with sulfur, further allowing the formation of few SO$_4^{2-}$ species in electrochemical reactions, which ends up passivating the surface of the electrode and hindering unwanted side reaction. Therefore, the Li-S electrochemical process, along with the support of alucone coating, completes a solid-phase electrochemical reaction, leading to higher potential polarization during the electrochemical reactions at room temperature. Some pioneer research using “small sulfur” cathode also enabled a reversible electrochemical reaction in carbonate electrolyte, which also claimed “solid-phase” Li-S reaction and the discharge-charge curves in their paper are consistent with our results [17]. Figure 8.4c shows the S K-edge spectra for pristine C-S electrodes in ether-based electrolyte as references and illustrates an alternative chemical structure evolution compared to sulfur cathodes cycled in carbonate-based electrolyte. During the discharge-charge process, the peak at 2472.2 eV doses not shift, indicating that polysulfides are dissolved in ether-based electrolyte. Further, the COSO$_2^-$ and SO$_4^{2-}$ peaks exhibit a reversible tendency during discharge-charge process, which can be attributed to the presence of LiTFSI salt (Figure S8.16) and the oxidation of sulfide species [34, 35]. Comparison of Figure 8.4a with Figures. 8.4b and 8.4c further demonstrates that a chemical interaction is taking place between the intermediate polysulfide species and alucone coating, and confirms the solid-state Li-S redox reaction with the support of alucone coating in carbonate-based electrolyte.

### 8.4 Conclusion

In summary, we have shown that the MLD alucone coating is a novel and potentially universal approach which enables safe high temperature Li-S batteries with conventional carbon-sulfur electrodes. The MLD alucone coated C-S electrodes demonstrate stabilized ultra-long cycle life at high temperature with a capacity over 570 mAh g$^{-1}$ after 300 cycles, representing the much stable and prolonged cycle performance for high-temperature Li-S
batteries. The utilization of MLD enables the usage of conventional carbon-sulfur cathode materials for Li-S batteries with carbonate based electrolytes, which is a facile and versatile approach that can be applied to a variety of C-S electrodes without re-designing the carbon host materials. It should be noted that the current MLD alucone coated C-S electrodes in carbonate based electrolyte still presents a number of challenges and unsatisfactory cycle performance at room temperature. These issues are related to the limited conductivity of the MLD coating, the nanostructure of the carbon host, and the components of carbonate based solvents. Our future work is aimed at further improving these portions of the Li-S batteries.

**Acknowledge**

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**References**


Power Sources 259 (2014) 289-299.


743.


[32] Lin, Z.; Liu, Z.; Fu, W.; Dudney, N. J.; Liang, C. Angew. Chem. 2013, 52, 7460-3;


Supporting information

**Figure S8.1** Comparison of (a) normal coating materials and (b) ALD/MLD coating for sulfur cathodes.

Different from normal coating deposited on composites, MLD and ALD processes enable a conformal coating thin film growth on as-prepared electrodes, which demonstrates the generality of MLD and ALD technology applied in sulfur cathodes and other electrode materials.

**Figure S8.2** Atomic layer deposition process on C-S electrodes.
Table S8.1 Physical properties of different electrolyte systems[1-3]

<table>
<thead>
<tr>
<th>Li Salt</th>
<th>Conventional Li-ion battery electrolyte (carbonate-based)</th>
<th>Conventional Li-S battery electrolyte (ether-based)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lithium hexafluorophosphate (LiPF₆)</td>
<td>Bis(trifluoromethane)sulfonimide lithium (LiTFSI)</td>
</tr>
<tr>
<td>Additive</td>
<td>No</td>
<td>LiNO₃</td>
</tr>
<tr>
<td>Solvents</td>
<td>Ethylene carbonate (EC)</td>
<td>Diethyl carbonate (DEC)</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>244-245</td>
<td>126-128</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>160</td>
<td>31</td>
</tr>
<tr>
<td>Auto ignition Point (°C)</td>
<td>465</td>
<td>445</td>
</tr>
</tbody>
</table>

*Data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa.)*
Figure S8. 3 FE-SEM image of carbon-sulfur electrode with scale bar 200 nm.

Figure S8. 4 FE-SEM images of C-S electrodes (scale bar 100 nm) with different MLD cycles of alucone coating (a) 2-cycle, (b) 5-cycle, (c) 10-cycle, and (d) 20-cycle. Scale bar 100 nm (a-d).
Figure S8. 5 TGA profiles of as-prepared C-S composites.

Figure S8. 6 (a) XRR spectra of alucone thin film with different MLD cycles on silicon film substrates, and (b) linearity of alucone thin film thickness vs. MLD cycle.

As shown in Figure S8.6b, the thickness of 10, 25, 50, and 100-cycle MLD alucone films were obtained by X-ray reflectivity measurement, demonstrating linear growth of alucone thin films on silicon substrate. The thickness of 10-cycle alucone coating is around 5.4 nm with a growth rate of around 0.57 nm/MLD cycle.
Figure S8. 7 (a) FTIR spectra and (b) sulfur 1s HEXPS spectra of alucone coated and pristine C-S electrodes.

Figure S8. 8 Sulfur 1s HEXPS spectra of alucone coated (a) and pristine (b) C-S electrodes.

SXRM beamline at CLS enables tunable photo energy in HEXPS measurement. The employed photo energy reflects the probing depth to samples, which allows us to obtain information from surface to bulk of sample. As shown in Figure S8.8a, the intensity of peaks at 2,475.0 eV varies from different photo energies in sulfur 1s spectra. The peak shows the highest intensity with 4,500 eV of photo energy (probing depth around 5 nm), while at 6,000 eV (probing depth 7-10 nm) the peak turns weak. It further confirmed the ultra-thin property of as-prepared alucone coating film and most of the interaction between sulfur and alucone coating occurred on the surface. Pristine C-S electrode is also conducted as references.
The thickness of coating directly effects on the performance of Li-S batteries in carbonate-based electrolyte. As shown in Figure S8.9, 5-cycle MLD coating and 10-cycle ALD coating still cannot help to realize a conventional electrochemical performance of batteries, which exhibit very low discharge capacities from the second cycle. With the cycle number increasing, MLD (10-cycle) and ALD (20-cycle) coating demonstrate their support on sulfur cathode, which shows drastical improvement in cycle performance. It indicates that the coating layer should be thick enough or covering enough for C-S electrodes. Further increasing the thickness of coating layer (MLD coating 20-cycle) will bring higher interfacial resistance in Li-S batteries which demonstrates a reversible but lower discharge capacity in cycle. Another interesting phenomenon is that the cycle performance from MLD coating is better than that of ALD coating, which we propose alucone coating layer may facilitate Li-ion diffusion than Al₂O₃ coating. The mechanisms of MLD and ALD coating need further investigation and more measurements to demonstrate in future.
Figure S8.10 Discharge-charge curves of (a) pristine C-S electrode in carbonate based electrolyte at room temperature; (b) alucone coated C-S electrode in carbonate based electrolyte; and (c) alucone coated C-S electrode in ether based electrolyte at high temperature.

A typical sulfur cathode in ether based electrolyte undergoes a two-step discharge process with Li metal, as shown in Figure S8.10c, corresponding to solid sulfur transferring to dissolved long-chain polysulfides (2.3 V, solid to liquid phase), followed by long-chain polysulfides further reducing to multiple short-chain sulfides (2.1 V, liquid to solid phase). However, the sulfur cathode in carbonate based electrolyte demonstrate an alternative electrochemical process. As shown in Figure S8.10a, due to the side-reaction of polysulfides and carbonate solvents, pristine C-S electrode are unable to complete a reversible Li-S electrochemical reaction. The alucone coated C-S electrode, on the other hand, undergoes a reversible electrochemical reaction with Li anode via an all-solid-phase process, which is only one potential plateau shown during discharge process.
Figure S8. 11 FE-SEM images of alucone coated C-S electrodes after electrochemical test under 55 °C (a) in carbonate based electrolyte; (b) in ether based electrolyte.

From images, it can be observed the electrolyte and separator turned yellow with the use of ether based electrolyte. The surface of electrode is also deposited a thick layer of discharge product, as shown in FE-SEM image. Nevertheless, the electrode operating in carbonate electrolyte maintain transparent liquid electrolyte and fewer discharge product deposition on the surface, demonstrating a stable cycling process of Li-S batteries with carbonate electrolyte running at high temperature.
Figure S8.12 EIS profiles of C-S electrodes in different electrolytes.

To gain insight toward the influence of the MLD coating on the conductivity of the electrode, 
electrochemical impedance spectra (EIS) was carried out. As shown in Figure S8.12a, 
the spectra of both pristine and alucone coated C-S electrodes consist of a semi-circle in the high 
frequency region and a straight line in the low frequency region. Both alucone coated and 
pristine electrodes display a small semicircle, indicating that the electrode with MLD coating 
maintains small surface charge-transfer resistance and high electrochemical activity. However, 
the alucone coating electrode also displays a short line between the semicircle and straight line 
(as indicated by the blue circle), which indicates an extra-interlayer existing as a result of the 
MLD coating and may be attributed to increased resistance toward Li-ion diffusion. Figure 
S8.12b shows the EIS profiles of electrodes in carbonate based electrolyte. Interestingly, the 
surface charge-transfer resistance of MLD coated electrodes is much smaller compared to 
pristine electrodes. Corresponding to electrochemical performance, the alucone coating can 
protect sulfur from side reaction with carbonate solvents and maintain high activity toward 
electrochemical reactions. The pristine C-S electrode may form a thick layer on the surface due 
to the side reactions, thereby making reversible Li-S reaction cycling unfavorable.
The coulombic efficiency of alucone coated C-S electrode, is only around 80 % and 90 % at room and elevated temperature, respectively. The wave of coulombic efficiency (red line) is due to the elevated temperature in test, leading to fast consumption of electrolyte. This unsatisfactory performance is predominately influenced by two factors. One is the carbonate electrolyte itself, which may be related to Li anode deposition and will be further optimized via employing additive in carbonate electrolyte to improve the performance [4, 5]. The second is the carbon host and coating material employed, which will undoubtedly influence performance of Li-S batteries. The carbon host we employed in this report is commercial mesoporous carbon and the conductivity of the alucone MLD coating is quite limited. We aim to develop a highly conductive MLD coating with advanced carbon host to further improve the performance of high temperature Li-S batteries.
Figure S8.14 Cycle performance of electrodes in different electrolytes at high temperature.
Figure S8. 15 XANES spectra of (a, c) references samples [6, 7] and (b) alucone coated C-S electrode at different electrochemical stages.
Figure S8. 16 Sulfur K-edge spectrum of LiTFSI salt.
Figure S8.17 Sulfur K-edge spectra of alucone coated C-S electrodes after discharge-charge cycles.
Figure S8. 18 Comparison of references with our work from Table S2.
**Table S8. 2** Summary of literature results and our work in high temperature Li-S batteries.

<table>
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<tr>
<th></th>
<th>Cycle performance (Discharge capacity)</th>
<th>Temperature</th>
<th>Electrolyte</th>
<th>Sulfur load</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Around 650 mAh g⁻¹/10th cycle at 0.1 C (only test 10 cycles)</td>
<td>45 °C</td>
<td>LiTFSI (DOL:DME:BTFE) Additive: LiNO₃</td>
<td>70 wt%</td>
<td><em>ACS applied materials &amp; interfaces</em>, 2014, <em>6</em>, 8006-8010</td>
</tr>
<tr>
<td>2.</td>
<td>Less than 250 mAh g⁻¹/50th cycles at 0.1 C</td>
<td>45 °C</td>
<td>LiTFSI (DOL:DME) Additive: LiNO₃</td>
<td>68 -75 wt%</td>
<td><em>J Power Sources</em>, 2014, <em>259</em>, 289-299</td>
</tr>
<tr>
<td>3.</td>
<td>Less than 250 mAh g⁻¹/150th cycles at 2 C</td>
<td>70 °C</td>
<td>LiTFSI (DOL:DME) Additive: LiNO₃</td>
<td>1.75 mg cm⁻²</td>
<td><em>J Power Sources</em>, 2013, <em>226</em>, 256-265.</td>
</tr>
<tr>
<td>4.</td>
<td>Less than 450 mAh g⁻¹/80th cycles at 1 C</td>
<td>60 °C</td>
<td>LiTFSI (DOL:DME)</td>
<td>66 wt%</td>
<td><em>Nano Energy</em>, 2013, <em>2</em>, 314-321</td>
</tr>
<tr>
<td>5.</td>
<td><strong>570 mAh g⁻¹/300th cycle at 0.1 C</strong></td>
<td>55 °C</td>
<td>LiPF₆ (EC:DEC:EMC)</td>
<td>65 wt%</td>
<td><strong>Our work</strong></td>
</tr>
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</table>
References


Chapter 9

9 Conclusion and Future Perspectives

This chapter summarized conclusions and contributions of this thesis, and personal statement and suggestions for future work were presented.

*Part of this chapter has been submitted to ACS Appl. Mater. Interfaces*
9.1 Conclusions

Rechargeable Li-S batteries have attracted great interests due to the ultra-high theoretical energy density. Compared with state-of-the-art Li-ion batteries, Li-S batteries are considered as the most promising energy storage systems applied for long-range electric vehicles and hybrid electric vehicles. However, Li-S batteries are still facing many challenges in practical application. Firstly, the insulation of sulfur and dissolution of polysulfides are two main issues of sulfur cathodes in Li-S batteries, which lead to low utilization of sulfur and reduced cycle life of Li-S batteries. Besides, the stability of electrolyte affects the safety of Li-S batteries. The ether based electrolyte has unstable physical properties at high temperature, which is not suitable for Li-S batteries in application. The carbonate based electrolyte results in side-reactions with polysulfides, which needs delicate nanostructure design in sulfur cathode to address it. Furthermore, lithium metal as anode material raises many challenges to this system, which needs deep understanding in the protection and utilization of lithium metal in future work.

This thesis work is mainly focused on the nanomaterials and nanostructure design for sulfur cathodes. A series of experimental designs were carried out in this study to fabricate various nanomaterials to construct sulfur cathodes for Li-S batteries. Different physical and electrochemical characterizations were conducted to determine the relationships of physical properties of as-prepared materials and electrochemical performance of Li-S batteries. Further, underlying mechanisms of materials and electrochemical reactions were explored, such as the relationships between heteroatom doping and discharge product deposition; porous structure of host materials and Li-S electrochemical reaction route; coating thickness effect and interaction of polysulfides; chemical bonding of coating layer and solid-phase Li-S reaction, etc. In summary, this study focused on sulfur cathodes in Li-S batteries and mainly works on three parts: nanomaterials fabrication, electrochemical characterization, and understanding of underlying mechanisms. The detailed study gained better understanding in Li-S batteries, and it is believed that these synthesis and analysis bring new sights of Li-S batteries in their applications.
Heteroatoms doped carbon black were synthesized via high temperature annealing treatment with different gas-phase atmospheres. The as-prepared carbon materials were tailored with designed porous structure and doping atoms. The three different heteroatoms doped carbon materials including nitrogen-doped, oxygen-functionalized, and bare carbon materials demonstrated different electrochemical performance in Li-S batteries. As determined by electrochemical and physical characterizations, it has been found that nitrogen doped carbon has improved conductivity, which is beneficial for sulfur utilization in electrochemical reaction. Further, nitrogen doped carbon also facilitates uniform deposition of discharge products, which shows highly reversible cycle performance of Li-S batteries. The study also applied synchrotron based XPS to understand the interactions between N-doped carbon with discharge products. The results showed that oxygen-functional groups have side-reactions with sulfur, which may cause dead regions in sulfur cathode and leads to deteriorate electrochemical performance of Li-S batteries.

TiN decorated carbon was synthesized via ALD and gas-phase post treatment. The as-prepared TiN demonstrated uniform deposition on porous carbon particles. Li-S batteries performance demonstrated the high electrical conductivity of TiN@C as carbon host for sulfur cathodes. Especially at high current density, the batteries presented stable and highly reversible discharge capacity in cycling, which is over two times of pristine carbon hosts.

Metal-organic framework derived carbon materials as a new family of carbon were successfully synthesized with controllable porous structure via gas-phase post treatment. The study demonstrates that with very short time NH$_3$ gas phase treatment under high temperature, it brings a variety of porous structure of MOF-C materials, and more importantly, these materials as carbon hosts for sulfur cathodes show different electrochemical reaction routes of Li-S batteries. The results illustrated that micropores enables to store short chain sulfur molecule and undergoes solid-phase electrochemical reaction in Li-S batteries. The mesoporous structure with longer NH$_3$ treating time presented higher utilization of sulfur cathodes and improved cycle performance of Li-S batteries. The study demonstrates a novel and facile synthetic approach to optimize porous structure of MOF-Cs, which gives a new sight for Li-S batteries and other energy storage systems with the use of different nanostructured carbon materials.
Coating is another attractive approach for sulfur cathodes to prevent side-reaction “shuttle effect”. The next parts present different coating materials via ALD and MLD to demonstrate variations of electrochemical performance and mechanisms of coating in Li-S batteries.

Ultrathin Al$_2$O$_3$ coating material for sulfur electrodes was successfully synthesized via atomic layer deposition technique (ALD). It demonstrated significantly improved cycle stability of sulfur cathodes with ALD Al$_2$O$_3$ coating. The study clearly claimed thickness effect of ALD coating layer on the electrochemical performance of sulfur cathodes, and concluded that the 2-cycle ALD Al$_2$O$_3$ performed the best cycle life for Li-S batteries. Further, the work also applied synchrotron based XPS to understand the coating effect during electrochemical process. It has been found that the ultrathin ALD Al$_2$O$_3$ coating layer partially transferred to LiAlO$_2$ and AlF$_3$ during charge and discharge, which can be considered as solid-state electrolyte and facilitate the Li-ion transportation into sulfur cathodes.

Following above work, molecular layer deposited alucone coating was further developed as coating material for sulfur cathode. The MLD alucone coating with improved mechanical properties has great benefit to accommodate sulfur cathode volume expansion in electrochemical reaction. The study demonstrated stabilized cycle capacity and prolonged cycle life of Li-S batteries with alucone coating. A comparison of MLD alucone coated with ALD Al$_2$O$_3$ coated and pristine sulfur electrodes was also carried out in this study.

At last, the work gave a new sight of the safety issue of Li-S batteries. With the use of MLD alucone coating, the study addressed a safe high-temperature Li-S batteries with prolonged cycle life. The alucone coating layer provides a stable environment for sulfur cathode in carbonate based electrolyte and enable sulfur cathode to undergo reversible Li-S reaction in this safe and stable electrolyte system. The study presented significantly improved cycle life of Li-S batteries with MLD coating under high temperature, and detailed mechanisms of coating effect were characterized with various of synchrotron based X-ray techniques. It has been found the alucone coating layer has interactions with
polysulfides to avoid side-reaction with carbonate solvents, which forms a solid-phase Li-S reaction in the carbonate based system. Therefore, the study resulted in a safe high temperature Li-S batteries with MLD coating layer.

9.2 Perspectives

Development of Li-S batteries is an important direction on the road of secondary high energy batteries. In this thesis, we summarized the design of carbon materials and development of coating materials for Li-S batteries. We will provide some suggestions for future work:

(1) For the sulfur cathode, various coating materials have been developed. However, very few coating designs have considered volume expansion of the electrode during electrochemical cycling. Yolk-shell and O-ring structures are successful architectures for the design of sulfur cathodes, and enable space for volume expansion resulting in prolonged cycle life for Li-S batteries. More advanced nanostructures based on these interface designs should be developed for the sulfur cathode with the protection of polysulfides while also improving electronic conductivity.

(2) With deeper understanding of Li-S batteries, an increasing number of researchers have moved toward the protection of the lithium anode. To address safe and high energy Li-S batteries, the effective utilization and protection of lithium metal is crucial. Although state-of-the-art lithium protection is limited due to the sensitive properties of lithium metal, a great number of novel and facile interlayer designs and detailed understanding on lithium electrochemical reactions are being carried out.

(3) ALD and MLD thin film technology are promising strategies in Li-S and Li-ion batteries. As summarized from the available literature, all of components related to interlayer design can use ALD and MLD techniques for Li-S batteries. The novel structure, precisely controllable thickness, as well as the facile operation process are very promising for designing an ideal coating material for Li-S batteries. Especially for lithium protection, ALD and MLD techniques will be further applied in Li-S and Li-ion batteries in the very near future.
In conclusion, Li-S batteries are considered as the most promising candidate for long-range EVs and HEVs. However, many challenges still hinder the development of high-energy Li-S batteries. Coating and interface design are very effective strategies in addressing the challenges that accelerate the commercialization of Li-S batteries. For sulfur cathodes, an effective coating enable the protection of polysulfides from dissolution and improve the conductivity of the sulfur cathode. For lithium metal, an artificial coating may facilitates a stable interface to prevent lithium corrosion and side-reaction with electrolytes. Further detailed research with advanced nanostructure design and in-situ characterization methods need to be developed for the study of this field.
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Publications:

(A) Peer-reviewed Journal Papers Based on This Thesis (First author)


4. **X. Li** and X. Sun, *Nitrogen-doped carbons in Li-S batteries: materials design and electrochemical mechanism*. Front. Energy Res. 49 (2014) 1


7. **X. Li** and X. Sun, *Interface design and coating materials applications of Li-S batteries*. ACS Appl. Mater. Interfaces, submitted

(B) Peer-reviewed Journal Papers Based on This Thesis (Coauthor)


(C) Previous publications


15. X. Li, C. Lai, C. W. Xiao, X. P. Gao, *Enhanced high rate capability of dual-phase Li$_4$Ti$_5$O$_{12}$-TiO$_2$ induced by pseudocapacitive effect* Electrochimica Acta 56 (2011) 9152

(D) Conference presentation and abstracts

1. Xia Li, Jian Liu, Xifei Li, Mohammad Banis, Biqiong Wang, Ruying Li, Mei Cai, and Andy X. Sun, *Development of Doped and Coated Cathodes for Highly Stable Li-sulfur Batteries*. 15th Topical Meeting of the International Society of Electrochemistry, Niagara Falls, 2014
2. **Xia Li**, Andrew Lushington, Jian Liu, Ruying Li, Andy X. Sun, *Development of Atomic and Molecular Layer Deposition Coated Cathodes for Highly Stable Lithium-Sulfur Batteries*. The International Conference on Electrochemical Energy Science and Technology, Vancouver Canada, 2015 *(Excellent oral presentation award)*


4. **Xia Li**, Andrew Lushington, Qian Sun, Jian Liu, Ruying Li, and Andy X. Sun, *Molecular scale coating and nanoscale carbon cage confined sulfur cathodes applied in Li-sulfur batteries*. 18th Intl. Meeting on Lithium Batteries, Chicago, 2016