

**Development of Nanostructured Cathode
Materials for Lithium-Sulfur Battery
Applications**

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DOCTOR OF PHILOSOPHY

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By

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work presented in this thesis has not previously been submitted for a degree or submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the I have written the thesis. Any help that I have received in my research work and the thesis's preparation has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This research is supported by an Australian Government Research Training Program.

Tuhin Subhra Sahu

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Dedicated to
My Parents

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Abstract

Over the last decade demand for renewable energy technologies has been one of the primary issues of concern across the globe. It is in this context, lithium-sulfur battery based on sulfur cathode have drawn the particular interest owing to the high specific capacity, high energy density and low cost of eco-friendly sulfur. Nonetheless, there are still formidable challenges hindering the successful application of lithium-sulfur battery. Those challenges can be categorized as, poor electrical conductivity of elemental sulfur, lithium polysulfide intermediate dissolution / shuttling. In my doctoral work, I focused mainly on the cathodes, such as developing a new class of sulfur material and optimizing the cathode structure to improve the electrochemical performance of lithium-sulfur batteries.

The first part of the thesis, we report a novel sulfur rich copolymer@ 3D graphene-carbon nanotubes (G-CNT) network cathode for high performance lithium-sulfur batteries. Unlike elemental sulfur as cathode, this squalene-derived copolymer can greatly suppress the dissolution of sulfur and polysulfides due to the chemical confinement from the crosslinking of polysulfur chains with the squalene molecules. While in the SP@G-CNT composite electrode, the interlinked Sp² G-CNT network not only enhance the polysulfide entrapment capability, but also provide the composite with an 3D electrically conductive path as well as an eminent mechanical resilience towards the huge volume change of sulfur. The as-developed cathode can deliver a high specific capacity, excellent rate performance and cycling stability.

In the second part, a nitrogen-doped micro/mesoporous carbon is derived from an amine-functionalized metal oxide framework (UIO-66-NH₂ abbreviated as NH₂-MOF) to host sulfur. Moreover, a freestanding permselective membrane was fabricated by the layer-by-layer (LBL) assembly of NH₂-MOF and graphene oxides nanosheets and implicated as an interlayer. Such,

multifunctional interlayer can block the shuttling of polysulfides in both physical and chemical ways without compromising the ion conductivity. The optimized lithium-sulfur cells realized high reversible capacity, extended cycling stability at high rate and much improved rate performance.

In the third part, a well-designed bilayer cathode structure is proposed to increase the active material loading and improve the areal capacity. The support layer contains carbon nanofiber / nickel nanoparticles decorated nitrogen-doped graphene (Ni-NG) and the top layer composed of Ni-NG nanosheets. The porous and highly conductive bilayer host not only ameliorates high sulfur loading and increase active material utilization but also accelerates the rapid conversion of polysulfides. With Li_2S_6 catholyte, bilayer Ni-NG@CNF cathodes demonstrates low voltage polarization, superior cycling stability and excellent rate performance.

Introduction

Lithium-Sulfur (Li-S) battery is one of the most promising candidates for the next-generation energy storage devices, with high specific capacity ($\sim 1672 \text{ mAh g}^{-1}$), high theoretical energy density (2600 Wh kg^{-1}) and low cost.^{1,2} However, the development and applications of Li-S battery have been severely hindered by the intrinsic poor electronic conductivity of sulfur and the rapid-capacity degradation due to dissolution of intermediate polysulfides into the electrolytes.³

Considerable efforts have been made to address the issues, including design of nanostructured cathode, optimization of electrolytes and protection of lithium anodes. One of the most common approaches in the cathode design is to utilize mesoporous carbonaceous materials as a potential host for sulfur.⁴ Typically, a highly conductive carbon matrix can improve the charge transfer resistance of the cathode and the mesopores within the structure can be used to trap soluble lithium polysulfides physically. However, weak interaction between hydrophilic lithium polysulfides and the non-polar carbon surface often leads to out-diffusion of polar lithium polysulfides over extended cycling.⁵ Recently, polar materials such as, hetero-atom doped carbon,^{6,7} metal oxides/sulphides/nitrides^{8, 9, 10} have been explored extensively. Unlike non-polar carbon, the hydrophilic surfaces of these polar hosts can bind the migrating lithium polysulfides via hydrophilic surface interaction and improve the cyclability of Li-S system. As a replacement for elemental sulfur, polymers containing high content of organosulfur that is covalently bonded to the organic backbones have also been reported as an effective strategy to endow both physical and chemical confinements on the soluble lithium polysulfides intermediates.¹¹ Therefore, in a nut-shell an ideal sulfur cathode host should have: (i) highly porous structure to encapsulate sulfur; (ii) high electronic conductivity to improve the active material utilization; (iii) capability to restrain

polysulfides and (iv) flexible and robust physical properties to buffer the volume change of active materials during lithium insertion/extraction.¹²

Chapter 1 introduces the research development of lithium-sulfur batteries. The working principle, major challenges, and the ongoing approaches to overcome these challenges are presented in this chapter.

Chapter 2 briefs about the experimental section, which includes material preparation techniques, physiochemical characterizations of as-prepared materials and their electrochemical investigations. Various synthesis strategies, such as solid-state reaction and hydrothermal synthesis were mainly applied to prepare different electrode materials in this doctoral work. This chapter also briefly introduces the instrumental analysis techniques that have been used to characterize the as-prepared electrode materials, including X-ray diffraction (XRD), Raman Spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), nitrogen adsorption-desorption, and Fourier transform infrared spectroscopy (FTIR). Cell assembly and electrochemical testing techniques, including cyclic voltammetry (CV) galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were also presented.

Chapter 3 presents synthesis of a novel sulfur-rich copolymer which is utilized as a new cathode active material for Li-S batteries. The sulfur-rich copolymer (87.29 % sulfur) synthesized by inverse vulcanization between two eco-friendly sources, sulfur and squalene. Covalent bonding between squalene (organic moiety) and sulfur molecules effectively suppresses the active material dissolution and migration during consecutive charge-discharge process. With such merit, the sulfur-rich copolymer (SP) demonstrates superior electrochemical performances as compared to that of elemental sulfur. For further improvement in electrochemical performances, SP was

combined with two-dimensional graphene (G) and three-dimensional graphene-carbon nanotubes (G-CNT) matrixes. The three-dimensional SP@ G-CNT composite shows high discharge capacity value (1265 mAh g^{-1} at 0.2 C), improved cycling stability (782 mAh g^{-1} at after 300 cycles at 1 C) and excellent rate performances compared to that of two-dimensional SP@G. This is attributed to the 3D interlinked Sp^2 G-CNT network, which not only improve the 3D electrically conductivity of the composite for better active material utilization, but also enhance the polysulfide entrapment capability and acts as a mechanical buffer against the huge volume change of active material.

Chapter 4 reports the synthesis of nitrogen-doped mesoporous carbon (NMC) with hierarchical pore architecture for high performance Li-S batteries. The materials contain nanopores ($< 2 \text{ nm}$) and mesopores ($2 - 4 \text{ nm}$), derived from carbonization of porous amine (NH_2)-functionalize metal organic frameworks (NH_2 -MOFs). Subsequently, sublimed sulfur was infused into the porous NMC by simple melt-diffusion method. Through the synergistic effect of nanopores and mesopores, the porous matrix can endow an exceptionally high ion-accessible surface area and low ion diffusion barrier. This conductive host not only improve the active materials utilization but also alleviate the large volume change of sulfur during electrochemical reaction. Besides, the successful N-doping can provide an additional interaction to the migrating lithium polysulfides. Exploiting the interaction between amidogen (NH_2) groups of NH_2 -MOFs and the surface functional groups of graphene oxide (GO), a layer-by-layer (LBL) assembled membrane (NH_2 -MOF-GO) was prepared by simple vacuum filtration technique and was utilized as an interlayer in between the cathode and the separator (PP). This freestanding permselective membrane can interact to the migrating lithium polysulfides in both physical and chemical ways. Therefore, the newly configured interlayer suppresses the polysulfide migration and ensure the lithium anode stability. As a result, compared with the NMC-S/PP, this rationally designed NMC-S/ NH_2 -MOF-

GO cell shows an obviously improved electrochemical performance, including discharge capacity and high-capacity retention.

Chapter 5 elucidates a sophisticated bilayer cathode structure to increase the sulfur loading, active material utilization, and the enhanced areal capacity. A simple vacuum filtration technique was adopted to fabricate the freestanding and flexible bilayer cathode. Bottom layer of this cathode consists of carbon nanofiber (CNF) and nickel nanoparticles decorated with nitrogen-doped graphene (NiNG). The top layer is composed of only NiNG. The integrated CNF and NiNG matrixes in the bottom layer host the active material and ensure their high utilization efficiency. Besides, intertwined CNF network possesses abundant void spaces to buffer the volume expansion of the active material. With the presence of nickel nanoparticles, the top NiNG layer accelerates the polysulfide conversion kinetics and effectively block the polysulfide migration. To maximize the potential of this bilayer host, Li_2S_6 / electrolyte solution (catholyte) was used as active material due well-dispersibility of the catholyte and drop-casted onto bottom layer of the bilayer host. Benefitting from such advantageous structural features, the bilayer Li_2S_6 -NiNG@CNF cathodes demonstrates low voltage polarization, improved cycling stability and excellent rate performance, including a reversible discharge capacity of 1272 mAh g^{-1} at 0.2 C rate, 89.4% capacity retention after 100 cycles and discharge capacity of 848 mAh g^{-1} at 3 C current rate. In addition, high sulfur loading up to 8 mg cm^{-2} and an areal capacity of 6.8 mAh cm^{-2} were achieved at low electrolyte to sulfur (E/S) ratio of $7 \mu\text{L mg}^{-1}_{\text{sulfur}}$.

Chapter 6 briefly summarizes the research outcomes of this thesis work and future perspective of cathode materials for Li-S batteries.