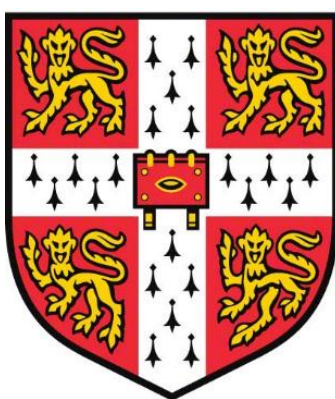


Development of New Cathodic Interlayers with Nano-Architectures for Lithium-Sulfur Batteries



Teng Zhao

Trinity College

Department of Materials Science and Metallurgy

University of Cambridge

*A Thesis Submitted in Fulfillment of the Requirements
for the Degree of Doctor of Philosophy*

November 2017

Declaration

This dissertation is the result of my own original work, and includes nothing which is the outcome of work done in collaboration except as acknowledged specifically in the text. This dissertation has not been submitted in whole or in part for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. The length of this dissertation does not exceed the prescribed word limit imposed by the Degree Committee of the Faculty of Physics and Chemistry.

Teng Zhao

Development of New Cathodic Interlayers with Nano-Architectures for Lithium-Sulfur Batteries

Teng Zhao

Abstract

Issues with the dissolution and diffusion of polysulfides in liquid organic electrolytes hinder the advance of lithium–sulfur (Li-S) batteries for next generation energy storage. To trap and re-utilize the polysulfides, brush-like, zinc oxide (ZnO) nanowires based interlayers were prepared ex-situ using a wet chemistry method and were coupled with a sulfur/multi-walled carbon nanotube (S/MWCNT) composite cathode. The cell with this configuration showed a good cycle life at a high current rate ascribed to (a) a strong interaction between the polysulfides and ZnO nanowires grown on conductive substrates; (b) fast electron transfer and (c) an optimized ion diffusion path from a well-organized nanoarchitecture. A praline-like flexible interlayer consisting of titanium oxide (TiO₂) nanoparticles and carbon (C) nanofiber was further prepared in-situ using an electrospinning method, which allows the chemical adsorption of polysulfides throughout a robust conductive film. A significant enhancement in cycle stability and rate capability was achieved by incorporating this interlayer with a composite cathode of S/MWCNT. These results herald a new approach to building functional interlayers by integrating metal oxides with conductive frameworks. The derivatives of the TiO₂/C interlayer was synthesized by changing the precursor concentration and carbonization temperature. Finally, a dual-interlayer was fabricated by simply coating titanium nitride (TiN) nanoparticles onto an electro-spun carbon nanofiber mat, which was then sandwiched with a sulfur/assembled Ketjen Black (KB) composite cathode with an ultra-high sulfur loading. The conductive polar TiN nanoparticles not only have a strong chemical affinity to polysulfides through a specific sulfur-nitrogen bond but also improve the reaction kinetics of the cell by catalyzing the conversion of the long-chain polysulfides to lithium sulfide. Besides, carbon nanofiber mat ensures mechanical robustness to TiN layer and acts as a physical barrier to block polysulfides diffusion. The incorporation of dual interlayers with sulfur cathodes offers a commercially feasible approach to improving the performance of Li-S batteries.

Acknowledgements

Firstly, I would like to express my deepest appreciation to my supervisor Dr R. Vasant Kumar for his enlightening mentorship through my PhD study in Cambridge from October 2014. Secondly, I'm indebted to all members of the Materials Chemistry Group for their sincere friendship and invaluable assistance, including Cheng-Yen Lao, Dr. Yingjun Liu, Dr. Kai Xi, Dr. Xiong He, Chenlong Gao, Dr Hyun Kyung Kim, Dr Paul Coxon, Dr Michael Coto, Dr Ali Kamali, Dr Sri Maha Vishnu Dunaboyina, Dr Jagdeesh Sure, Siti Norbaya Ahmad Nor, Varun Choda, Amir Fakeeh, Dr Robert Liu, Maina Poterlla Garcia, Dr Chris Harris and Peter Knight. They all helped in different ways and I had an enjoyable time with them over the three years. Especially, I extend my hearty thanks to Cheng-Yen Lao, who is always here when I am in trouble. Without his support and advice, this research would not have been done. Appreciations also go to Dr. Xiaoyu Peng, Dr. Giorgio Divitini and Dr. Caterina Ducati for their help with electron microscopy. I would also like to acknowledge the collaboration with Yusheng Ye and Prof. Renjie Chen from Beijing Institute of Technology for making my PhD productive and I really appreciate the support of the Krishnan-Ang Studentship from Trinity College. Last but not least, I would like to express my gratitude to my dear parents for all their encouragements in my life.

T.Z.

There is Plenty of Room at the Bottom

Richard Feynman

Table of Content

Declaration	ii
Abstract	iii
Acknowledgements	iv
Chapter 1 Introduction	1
1.1 Aims and Thesis Structure	2
1.2 Administrative and Organizational Aspects.....	4
1.2.1 PhD Supervision	4
1.2.2 Research Laboratory, Collaborations and Contributions	4
Chapter 2 Literature Review	5
2.1 Lithium-Sulfur Batteries at a Glance	5
2.2 Electrochemistry.....	7
2.3 Technical Challenges	9
2.4 A Nano Approach to Better Utilization of Sulfur Species	9
2.4.1 Cathodes	10
2.4.2 Interlayers	32
2.5 The Specific and Volumetric Energy of Li-S Batteries at Laboratory Scale	41
Chapter 3 Characterization Techniques	43
3.1 X-ray Powder Diffraction (XRD)	43

3.2 Raman Microscopy	44
3.3 Thermogravimetric Analysis.....	44
3.4 Scanning Electron Microscopy (SEM)	44
3.5 Transmission Electron Microscopy (TEM).....	45
3.6 X-ray Photoelectron Spectroscopy (XPS).....	46
3.7 Gas Sorption and Textural Characterization	46
3.8 Electrochemical Measurements.....	47
 Chapter 4 A Bio-inspired Polysulfides Adsorptive Interlayer Made from Zinc Oxide	
Nanowires for a Sulfur/Carbon Nanotube Cathode	50
4.1 Overview of the Work.....	50
4.2 The Methods.....	51
4.2.1 Chemical Bath Deposition of ZnO Nanowire Arrays on Nickel Foam.....	51
4.2.2 Thermal Infusion of Sulfur on the Surface of MWCNT	51
4.2.3 Fabrication of Electron-spun PAN Derived Carbon Nanofiber	51
4.2.4 Growth of ZnO Nanowires on Carbon Nanofiber	52
4.2.5 Theoretical Calculation.....	52
4.3 Microstructure and Morphology Characterization	53
4.3.1 Multi-walled Carbon Nanotube/Sulfur Composite Cathode	53
4.3.2 Zinc Oxide/Nickel Foam Interlayer.....	58
4.3.3 Zinc Oxide/Carbon Interlayer.....	62

4.4 Electrochemical Test and Postmortem Analysis	67
4.4.1 A Proof of Concept.....	67
4.4.2 A Light-Weight Battery	76
4.5 Summary of this Chapter.....	81
Chapter 5 A Praline-Like Flexible Interlayer with Highly Mounted Polysulfide Anchors for a Sulfur/Carbon Nanotube Cathode	82
5.1 Overview of the Work.....	82
5.2 The Methods.....	83
5.2.1 Electrospinning of TiO ₂ -PVP Nanofiber Precursor.....	83
5.2.2 Carbonization of TiO ₂ -PVP Nanofiber Precursor	83
5.2.3 Theoretical Calculation.....	83
5.3 Microstructure and Morphology Characterization	84
5.3.1 TiO ₂ /PVP Composite Precursor	84
5.3.2 TiO ₂ /C Composite	85
5.4 Electrochemical Test and Postmortem Analysis	91
5.5 The Derivatives of TiO ₂ /C Composite	97
5.6 Summary of this Chapter.....	102
Chapter 6 A Dual-Interlayer Consisting of Carbon and Titanium Nitride for an Oval-Like Carbon/Sulfur Cathode	103
6.1 Overview of the Work.....	103

6.2 The Methods.....	104
6.2.1 Synthesis of an Oval-Like Carbon/Sulfur Composite Cathode.....	104
6.2.2 Fabrication of TiN based Dual-Interlayers.....	104
6.3 Microstructure and Morphology Characterization.....	105
6.3.1 A Oval-Like Carbon/Sulfur Composite Cathode	105
6.3.2 Titanium Nitride/Carbon Interlayer.....	110
6.4 Electrochemical Test and Postmortem Analysis.....	113
6.5 Summary of this Chapter.....	118
Chapter 7 Overall Conclusions and Future Directions	119
7.1 Conclusions	119
7.2 Future Directions.....	121
Bibliography	123

List of Figures

Figure 1.1: Comparison of Energy Density of Li-S and Li-Ion Batteries ^[6]	2
Figure 2.1: Evolution of Battery Energy Density over Years ^[8]	5
Figure 2.2: Statistics of Publications of Li-S Batteries in Recent Years (Web of Science, 2017 still in progress).....	7
Figure 2.3: Illustration of the Multi-Step Electrochemical Mechanism Involved in a Typical Li-S Battery, Consisting of a S Cathode, Organic Electrolytes and a Li Anode.	8
Figure 2.4: (a, b) TEM Images of S/OMC Composites with Different Magnification;(c, d) Elemental Mapping of C and S; (e) Schematic of S/OMC Composite; (f) Discharge-Charge Profile of S/OMC Composites; (g) Cycle-Performance Comparison Of OMC/S-PEG (Upper Points, In Black) Versus S/OMC (Lower Points, In Red) ^[101]	10
Figure 2.5: (a) TEM Image, (b) Cycle Performance and (c) Schematic of S/MMCS Composite ^[105]	12
Figure 2.6: (a) Scheme of S Molecules Confined in Micropores; (b) TEM Image of S-CNT@MPC Composite; (c) N ₂ Adsorption/Desorption Isotherms of S-CNT@MPC and CNT@MPC Composite; (d) Charge-Discharge Profile of S-CNT@MPC Composite at Different Cycles ^[106] .13	
Figure 2.7: (a) TEM Images and (b) Cycle Life of S@C sphere Composites; (c) STEM Images of NHC-S Composite; (d-e) Elemental Mapping of C and S; (f) Cycle Performance ^[109]	14

Figure 2.8: (a, d) Scheme of the composite structures; (b, e) TEM and SEM images; (c, f) Cycle performance of S/graphene and graphene-S/PEG Composites ^[116,117]. 15

Figure 2.9: (a) Schematic of a Heterogeneous Crystal Growth Mechanism of S particles on HF-treated Graphene; (b) TEM Image of S/HF-Treated Graphene Composite; (c) Cycle Performance^[119]. 16

Figure 2.10: (a) Scheme for the Synthesis of Unstacked DTG; (b) Cycle-Performance of S-DTG at Different Rates^[121]. 17

Figure 2.11: Schematic for the Preparation of Self-Weaving S/MWCNT Cathode^[124]. 18

Figure 2.12: Model of the Discharge–Charge Process of S/MWCNT Nano/Microsphere with Hierarchical Architecture^[127]. 19

Figure 2.13: (a,d) SEM images; (b,e) Electrochemical Performance; (c,f) Structural Scheme of Sandwich Structured G-MWCNT@S and S-G/SWCNT/Composite^[128]. 20

Figure 2.14: (a) Schematic Illustration of the Fabrication of MNCS/CNT Composite; (b) SEM Image of MNCS/CNT Composite; (c) Comparison of the Ability of Various Adsorbents in Absorbing Polysulfides^[131]. 21

Figure 2.15: (a) Schematic Illustration of the Fabrication of the NDHCS–S Composite and G–NDHCS–S Hybrid Paper; (b) Cross-Section SEM Image of G–NDHCS–S Hybrid Composite; The Corresponding Elemental Mapping of S (c), C (d) And N (e); (f) Cycling Performance and Coulombic Efficiency of The G–NDHCS–S And G–S Electrodes^[50]. 22

Figure 2.16: (a,b) Schematic of the Concept of the ‘Polysulfide Reservoir’ Afforded by SBA-15 and TiO_2 Embedded in S/C Composite; (c,d) Effect of SBA-15 and TiO_2 Incorporation on the Cycle Performance of S/OMC Cathode^[135] 24

Figure 2.17: (a) Schematic of the Formation Process; (b) TEM Images; (c) The Particle Size Distributions; (d) Electrochemical Performance of Yolk–shell S@ TiO_2 Composite^[139] 25

Figure 2.18: (a) SEM and (b) Schematic of TiO_{2-x} Inverse Opal after S Infusion; (c) Electrochemical Performance of TiO_{2-x} /S Composite^[140]. 26

Figure 2.19: (a) Schematic and (b) TEM Image of ITO/CNF Composite; (c) Cycle-Performance of S/ ITO/CNF Composite^[142]. 27

Figure 2.20: (a) S@PTh Composite^[143]; (b) Nano S@PEDOT Composite^[144]; (c) Hollow S@PVP Composite^[145]; (d) S@MWCNT-PNAi Composite^[146]. 28

Figure 2.21: (a) Schematic of the Formation Process; (b) TEM Images; (c) The Particle Size Distributions; (d,e) Electrochemical Performance of Yolk–Shell S@PANi Composite^[148] 30

Figure 2.22: Illustration of the Construction and Discharge/ Charge Process of the SPANi-NT/S Composite. 30

Figure 2.23: Scheme for the Li-S Batteries with a Bi-functional Microporous Carbon Interlayer^[151]. 32

Figure 2.24: (a) Schematic of Li-S Batteries with a Carbon Paper Interlayer; (b) Comparison of Cycle Performance of Sulfur Cathode with Different Interlayers; (c) Scheme for the Surface Modification of Carbon Paper by NaOH Treatment; (d) FT-IR Spectrum of Carbon Paper before and after NaOH Treatment^[69]. 33

Figure 2.25: Comparison of Cycling Performance of Li-S Batteries with Varying Thicknesses of Activated CNF Interlayers.	34
Figure 2.26: Illustration of the Function of TiO ₂ /CNT paper Interlayer ^[155]	35
Figure 2.27: DFT Calculation of Binding Energies of Li-S• with (a) ZnO and (b) MgO ^[158]	36
Figure 2.28: (a) Cross-Section SEM Image of TiO ₂ /TiN-Graphene Interlayer; (b) Scheme for the Twin-Born TiO ₂ /TiN Heterostructures on Graphene; (c) Cycle Performance of Batteries with TiO ₂ / TiN-Graphene Interlayer ^[73]	37
Figure 2.29: (a) Schematic of A Lithium-Sulfur Battery with the Incorporation of A GO Membrane; (b) Cross-Section SEM Image of GO Membrane; (c) Comparison of Cycle Performance of Batteries with and without GO Membrane ^[160]	38
Figure 2.30: (a) Polysulfide Permeation Measurements for MOFs/GO (Upper) and GO (Lower) Membrane; (b) Comparison of Cycle Performance of Batteries with MOFs/GO and GO Membrane; (c) SEM Image of MOFs/GO Membrane ^[162]	39
Figure 2.31: (a) Photograph and (b) TEM Images of the PPy Nanotubes; (c) A Schematic for the Rechargeable Li-S Batteries with the PPy Nanotube Interlayer ^[164]	40
Figure 2.32 The Configuration of Li-S Batteries at Laboratory Scale	42
Figure 3.1: Bragg Diffraction Scheme.	43
Figure 3.2: Schematic of Beam and Specimen Interaction and Signals Emitted From Different Parts of the Interaction Volume.	45

Figure 3.3: Five Different Types of Adsorption Isotherm.	47
Figure 3.4: Schematic for a Common Nyquist Plot.	48
Figure 4.1: (a) Low and (b) High magnification SEM images of S/MWCNT Composite Cathode.	53
Figure 4.2: XRD Spectra of S/MWCNT Composite, S and MWCNT.	54
Figure 4.3: Raman Spectra of S/MWCNT Composite, S and MWCNT.	55
Figure 4.4: Photograph (Inset) and Cross-Section SEM Image of S/MWCNT Composite Cathode with a S Loading of $3\text{mg}/\text{cm}^2$	56
Figure 4.5: TGA Curves of S/MWCNT Composite, S and MWCNT.	57
Figure 4.6: Illustration of the Advantages of 1D Nanowire Arrays on Current Collector ^[178]	58
Figure 4.7: Illustration of the Effect of PEI during Synthesis of ZnO Nanowires ^[182]	59
Figure 4.8: XRD Spectrum of ZnO Nanowire/Ni Foam Interlayer.	60
Figure 4.9: Top-View (a) And (b) Cross-Section Low Magnification SEM Images of the Hybrid ZnO Nanowires/Ni Foam Interlayer; (c-e) High-Magnification SEM Images of the Hybrid ZnO Nanowires /Ni Foam Interlayer; (f) Secondary Electrons (SE) SEM Image of The Hybrid ZnO/Ni Interlayer and the Corresponding Elemental Maps.	61
Figure 4.10: Schematic for the Set-up of Electrospinning.	62

Figure 4.11: Photographs of PAN Precursor (White) and Stabilized PAN (Brown); The Structure Conversion of PAN During Stabilization Process.	63
Figure 4.12: Photographs of Carbonized PAN Nanofiber Mats.	63
Figure 4.13: (a, b) Cross-Section of Low and High Magnification SEM Images of the Carbon Nanofiber Interlayer. Top-View Low and High Magnification SEM Images: (c,d) The Carbon Nanofiber Interlayer; (e,f) The Hybrid ZnO Nanowires/C Nanofiber Interlayer.	64
Figure 4.14: (a) Nitrogen Adsorption Isotherms and (b) Pore Size Distribution of ZnO Nanowire/Carbon Nanofiber Interlayer and Carbon Nanofiber.	65
Figure 4.15: TGA Curves of ZnO Nanowires/Carbon Nanofiber Interlayer.	66
Figure 4.16: XRD Spectrum of ZnO Nanowire/Carbon Nanofiber Interlayer.	66
Figure 4.17: CV Plots of the Li-S Cell with Different Interlayers: (a) ZnO Nanowires/Ni Foam; (b) Ni Foam; (c) No Interlayer.	67
Figure 4.18: Discharge–Charge Profiles of the Li-S Cell with Different Interlayers after Different Cycles at 0.2C: (a) ZnO/Ni Foam; (b) Ni Foam; (c) No Interlayer; (d) Comparison of Cycle Performance of S/MWCNT Cathode with Different interlayers at a Current Density of 0.2C within a Potential Window of 1.8-2.6 V Versus Li/Li ⁺ for 50 Cycles.	68
Figure 4.19: (a) Comparison of Rate Performance of Li-S Cell with Different Interlayers at Different Current Rates; (b) Nyquist Plots of Li-S Cell with Different Interlayers Measured Before Cycling.	70
Figure 4.20: Nyquist Plots of Li-S Cell with Different Layers Measured before Cycling.	71

Figure 4.21: Cycle Performance of the Li-S Cell with ZnO Nanowires/Ni Foam Layer at High Current Rates. 72

Figure 4.22: (a) Low Magnification SEM Image of the Cycled Hybrid Interlayer and Corresponding Elemental Mappings (Inset: High Magnification SEM Image); (b) TEM Image of Cycled ZnO Nanowires; (c) TEM Image of A Single ZnO Nanowire with a Rough S-Containing Shell and Corresponding Elemental Maps..... 73

Figure 4.23: (a) XPS Survey Spectra of Hybrid Layer before and after Cycling; (b) S2p XPS Spectrum of the Cycled Hybrid Layer; (c) Comparison of Zn 2p_{3/2} XPS Spectrum of the Hybrid Layer before and after Cycling; (d) Optimized Configurations for the Binding of Five S Species to The O-Terminated Polar Surface of Wurtzite ZnO Crystal..... 75

Figure 4.24: Nyquist Plots and the Equivalent Circuit (Inset) for the S/MWCNT Composite Cathode with Different Interlayers. 76

Figure 4.25: (a) Cycle Performance of the Li-S Cell with Different Interlayers at a Current Rate of 0.2C. Discharge–Charge Profiles of the Li-S Cell with Different Interlayer after Different Cycles at 0.2 C; (b) ZnO/C; (c) C Interlayer. 77

Figure 4.26: CV Curves of S/MWCNT Composite Cathodes with Different Interlayers at a Scan Rate of 0.1mV/s: (a) ZnO Nanowires/Carbon Nanofibers Interlayers; (b) Carbon Nanofibers Interlayers. 78

Figure 4.27: (a) Cycle Performance of the Li-S Cell with Different Interlayers at a Current Rate of 1C: Discharge–Charge Profiles of the Li-S Cell with Different Interlayer after Different Cycles at 1C; (b) ZnO/C; (c) C Interlayer. 79

Figure 4.28: (a) Schematic of the Structural and Chemical Function of the Hybrid ZnO Nanowires/Carbon Nanofibers Interlayer in Li-S Batteries; SEM Image of the Cycled Hybrid ZnO

Nanowires/Carbon Nanofibers Interlayer and Corresponding Elemental Map: (b) Cathode Side; (c) Separator Side.	80
Figure 4.29: EDS Spectra for the Cycled ZnO/C Interlayer: (a) Facing Cathode Side; (b) Facing Anode Side.....	81
Figure 5.1: (a) Snapshots of TiO ₂ /PVP Interlayer at Different Bending Angle; (b) SEM Image of TiO ₂ /PVP Precursor.	84
Figure 5.2: (a) Photographs of the As-Prepared TiO ₂ /C Interlayer; (b) Snapshot of TiO ₂ /C Interlayer at Different Bending Angle; (c-d) Low and High Magnification Cross-Sectional SEM Images Of TiO ₂ /C Interlayer; (e, f) Top-View and Cross-Section SEM Images of TiO ₂ /C Interlayer.	85
Figure 5.3: (a-c) Low and High Magnification TEM Images of TiO ₂ /C Nanofibers.	86
Figure 5.4: STEM Image of a TiO ₂ /C Nanofiber and Corresponding Elemental Maps.....	86
Figure 5.5: XRD Spectrum of TiO ₂ /C Interlayer.....	87
Figure 5.6: (a) Nitrogen Adsorption Isotherms and (b) Pore Size Distribution of TiO ₂ /C Interlayer.	88
Figure 5.7: TGA Curve of TiO ₂ /C Interlayer.....	89
Figure 5.8: (a) Low and (b) High Magnification SEM Images of Samples after TGA; (c) The Corresponding Elemental Maps.....	90
Figure 5.9: XRD Spectrum of Samples after TGA.....	90

Figure 5.10: Comparison of Cycle-Performance of Sulfur/Carbon Nanotubes Composite Cathode with Different Interlayers at a Current Rate of 0.2C.	91
Figure 5.11: Discharge-Charge Profiles of S/MWCNT Composite with (a) TiO ₂ /C Interlayer and (b) No Interlayer.	92
Figure 5.12: Rate-Performance of S/MWCNT Composite with (a) TiO ₂ /C Interlayer and (b) No Interlayer.	92
Figure 5.13: (a) Rate Performance Discharge-Charge Curves of the S/MWNCT Cathode with TiO ₂ /C Interlayer at Different Current Rates; (b) Discharge-Charge Curves of the S/MWNCT Cathode with No Interlayer at Different Current Rates.	94
Figure 5.14: Nyquist Plots of AC Impedance Spectra of S/MWNCT Cathode with Different Interlayers.	94
Figure 5.15: STEM Images of Cycled TiO ₂ /C Interlayer with Corresponding Elemental Maps.	95
Figure 5.16: SEM Images of the Fresh Cycled TiO ₂ /C Interlayer with Corresponding Elemental Maps: (a) Facing Cathode Side; (b) Facing Anode Side.	95
Figure 5.17: (a) Comparison of Ti _{2p} XPS Spectrum of the Hybrid Interlayer before and after Cycling; (b) S _{2p} XPS Spectrum of the Cycled Interlayer.	96
Figure 5.18: Configurations for the Binding of Five S Species on Rutile-TiO ₂ (110) Surface.	96
Figure 5.19: SEM Images of Electrospun TiO ₂ /C Nanofibers Using Different PVP Concentration: (a, d) 0.03 g ml ⁻¹ ; (b, e) 0.05 g ml ⁻¹ ; (c, f) 0.07 g ml ⁻¹	97

Figure 5.20: Electrospun TiO_2/C Nanofibers Using Different PVP Concentration: (a) XRD Patterns; (b) Nitrogen Sorption Isotherms and (c) Pore Size Distribution Calculated from the Desorption Branch.	98
Figure 5.21: Low and High Magnification SEM Images of TiO_2/PVP Precursor after Carbonization at Different Temperature: (a, b) $800\text{ }^\circ\text{C}$; (c, d) $900\text{ }^\circ\text{C}$, (e, f) $1000\text{ }^\circ\text{C}$	99
Figure 5.22: XRD Patterns for the TiO_2/PVP Precursor after Carbonization at Different Temperature.	100
Figure 5.23: (a) Nitrogen Sorption Isotherms and (b) Pore Size Distribution Calculated from the Desorption Branch.	101
Figure 6.1: Low and High Magnification SEM Images of the Assembled KB.	105
Figure 6.2: SEM Image Assembled KB/S Composite.	106
Figure 6.3: TGA Curves of Assembled KB/S Composite and Sulfur.	106
Figure 6.4: N_2 Adsorption/Desorption Isotherm Curves of Assembled KB and Assembled KB/S Composite.	107
Figure 6.5: XRD Patterns of Sulfur, Assembled KB and Assembled KB/S Composite.	108
Figure 6.6: Cross-Section SEM Image of Assembled KB/Sulfur Composite Cathode.	108
Figure 6.7: (a, b) Low and c) High Magnification SEM Images of TiN/C Interlayer and (d) Elemental Mapping.	110

Figure 6.8: The Cross-Sectional SEM Images of TiN/C Interlayer and the Corresponding EDS Mapping and Spectrum.	111
Figure 6.9: XRD Pattern of TiO ₂ /C Interlayer.	112
Figure 6.10: Raman Spectrum of TiN/C Interlayer.	112
Figure 6.11: Cycle Performance of the Li–S Cell with Different Interlayers at a Current Rate of 0.1C: (a) TiN/C Interlayer; (b) Carbon Interlayer.	113
Figure 6.12: Discharge–Charge Profiles of the Li–S Cell with Different Interlayers at Current Rate of 0.1C: (a) TiN/C Interlayer; (b) Carbon Interlayer.	114
Figure 6.13: Cycle Performance of the Li–S Cell with Different Interlayers at a Current Rate of 0.2C: (a) TiN/C Interlayer; (b) Carbon Interlayer.	114
Figure 6.14: Discharge–Charge Profiles of the Li–S Cell with Different Interlayers at a Current Rate of 0.2C: (a) TiN/C Interlayer; (b) Carbon Interlayer.	115
Figure 6.15: (a) Low and (b) High Magnification SEM Images of Cycled TiN/C Interlayer; (c) EDS Mapping of the Cycled TiN/C Interlayer.	116
Figure 6.16 : (a) XPS Survey Spectra of TiO ₂ /C Interlayer before and after Cycling; (b) S _{2p} XPS Spectrum of The Cycled Interlayer; (c) Comparison of Ti _{2p} ; (d) N _{1s} XPS Spectrum of the Hybrid Interlayer before and after Cycling.	117

List of Abbreviations

BET	B runauer- E mmett- T eller
CNF	C arbon N anofiber
CNT	C arbon N anotube
CV	C yclic V oltammetry
DFT	D ensity F unctional T heory
DTG	D ouble-layer T emplated G raphene
EDS	E nergy- d ispersive X -ray S pectroscopy
EIS	E lectrochemical I mpedance S pectroscopy
FT-IR	F ourier- t ransform I nfrared S pectroscopy
G	G raphene
GO	G raphene O xide
HGNs	H ollow G raphene N anoshells
KB	K etjen B lack
LIB	L ithium I on B atteries
MMCS	M eso-microporous C arbon S phere
MNCS	M esoporous N itrogen-doped C arbon S phere
MOFs	M etal O rganic F rameworks
MPC	M icroporous C arbon
MWCNT	M ulti-walled C arbon N anotube
NDHCSs	N -doped D ouble-shelled H ollow C arbon S pheres
NHC	N itrogen-doped H ollow C arbon
NMP	N - M ethyl-2- p yrrolidone
OMC	O rdered M esoporous C arbon
PAA	P oly(a cylic a cid)
PAN	P olyacrylonitrile
PEDOT	P oly (3,4-ethylenedioxythiophene)
PANi	P oly a niline

PDA	P oly d opamine
PEG	P olyethylene- g lycol
PP	P oly p ropylene
PPy	P oly p yrrole
PTh	P oly t hiophene
PVDF	P olyvinylidene f luoride
PVP	P olyvinyl p yrrolidone
SBA-15	Santa B arbara A morphous- 15
SEM	Scanning E lectron M icroscopy
SWCNT	Single-walled C arbon N anotube
TEM	T ransmission E lectron M icroscopy
TGA	T hermal G ravimetric A nalysis
XPS	X -ray P hotoelectron S pectroscopy
XRD	X -ray D iffraction

Chapter 1 Introduction

Batteries are currently one of the most important power sources in our daily life and serve in a diverse range of applications from portable devices to large-scale utilities. Historically, the term “batteries” was initially used by Benjamin Franklin in 1748 to describe assembled Leyden jars, which are actually a set of linked capacitors^[1]. About fifty years later (1799), Alessandro Volt, invented the first-ever battery that generated a constant current through an external circuit. It was constructed by a pile of alternating discs of copper and zinc that were separated by pasteboard discs soaked in brine. Generally, batteries are closed systems and are composed of two electrodes immersed into an electrolyte. The electrical energy is produced by the conversion of chemical energy via redox reactions at the electrode/electrolyte interface. Compared with the energy from the combustion of fossil fuels, electrochemical energy produced by reusable materials is more environmentally friendly and is envisioned as the sustainable road to the future^[2].

With the industrial revolution and technological innovation over the last two centuries, batteries with different electrochemical couples have been developed, including lead-acid, nickel-cadmium and lithium ion batteries^[3]. Among them, lithium-ion batteries (LIBs) have been considered the most common secondary batteries since their first commercialization by Sony Company in 1991^[4]. Based on a topotactic intercalation mechanism, LIBs offer a theoretical specific energy of ~ 400 Wh kg^{-1} for lithium transition-metal oxide/graphite systems and have good cycle life and high Coulombic efficiency. Accordingly, LIBs have become a near-ubiquitous battery technology and dominated portable electronic markets for almost 30 years. As battery technology moves beyond conventional lithium-ion chemistries, batteries based on lithium-sulfur (Li-S), are now increasingly earmarked as a viable means to meet the demands of long-term and robust energy storage applications^[5]. Owing to a nontopotactic “assimilation” process, Li-S batteries afford a theoretical specific energy about five times greater than LIBs (**Figure 1.1**). Besides, the non-toxic nature and abundance of elemental S are also attractive in terms of large-scale production and sustainable development, which is a crucial factor in mass deployment of electrical vehicles^[6].

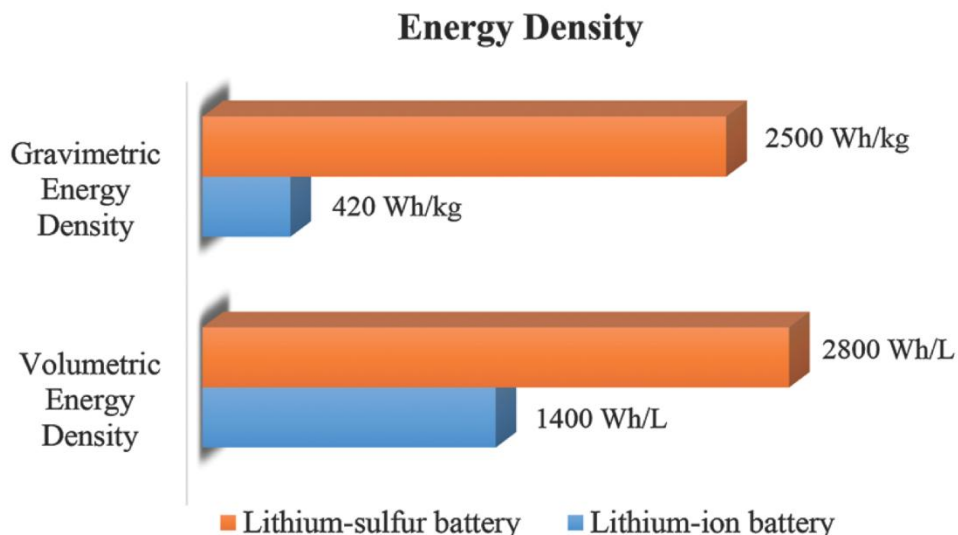


Figure 1.1: Comparison of Energy Density of Li-S and Li-Ion Batteries^[6].

The technology shows promise and stands on a commercial cusp, but if the large-scale uptake of Li-S batteries is to be fully realized, several fundamental hurdles must be overcome. One especially critical factor is the sharp capacity drop brought about by the dissolution and diffusion of polysulfides in the organic electrolyte. This causes the active material to be lost and limits the battery lifetime.

1.1 Aims and Thesis Structure

This PhD project aims to address the aforementioned critical hurdle by placing nanostructured interlayers on top of sulfur cathodes in order to physically and/or chemically adsorb these active materials and keep them electrochemically reusable. The experimental work carried out in this thesis was primarily structured towards potentially commercially viable applications of Li-S batteries. Specifically, a sulfur/multi-walled carbon nanotube composite (S/MWCNT) with a relatively low sulfur loading was initially coupled with a brush-like zinc oxide (ZnO) based interlayer prepared ex-situ using a wet chemistry method, which was then replaced with a praline-like titanium oxide (TiO₂) based interlayer fabricated in-situ using an electrospinning method. Finally, a sulfur/assembled Ketjen black (KB) composite with a high sulfur loading was sandwiched with a dual interlayer prepared by simple coating of titanium nitride nanoparticles on carbon nanofiber mat. The structural and chemical effects of the interlayers on the performance of cathodes were investigated by postmortem analysis. And insights into the interaction mechanism between active materials and interlayers were also presented by theoretical calculation.

The thesis summarizes my research discoveries during the PhD project on the topic of “*Development of New Cathodic Interlayers with Nano-Architectures for Lithium-Sulfur Batteries*”.

It is structured as follows:

- Chapter 1: introduces a basic background and aim of the PhD project as well as the structure of the PhD thesis.
- Chapter 2: begins with an overview of Li-S batteries, covering the historical development, fundamental mechanism, potentials and challenges. The chapter also outlines the advances in nanostructured cathodes and interlayers for Li-S batteries.
- Chapter 3: constitutes the characterization techniques involved in the experimental work and give a brief introduction of their working mechanism and conditions.
- Chapter 4: the assessment of a bio-inspired brush-like interlayer made from ZnO nanowires and conductive frameworks to improve the performance of a S/MWCNT composite cathode. The chemical effect of ZnO on capturing polysulfides was investigated, initially by using a commercially-available nickel foam as a conductive scaffold, which was then replaced by a lightweight electro-spun carbon nanofiber mat for practical application.
- Chapter 5: the assessment of a praline-like interlayer consisting of TiO₂ nanoparticles and carbon nanofibers to improve the performance of a S/MWCNT composite cathode. The spatial distribution of TiO₂ over the carbon fiber was characterized and its structural effect on the performance of a S/MWCNT composite cathode was investigated. Moreover, the derivatives of TiO₂/C composite was synthesized by changing precursor concentration and carbonization temperature.
- Chapter 6: the assessment of a dual-interlayer constructed by layered TiN nanoparticles and carbon nanofibers to improve the performance of a S/assembled KB composite cathode with an ultra-high sulfur loading. The effect of TiN on the performance was investigated by using a pure carbon nanofiber interlayer as a reference.
- Chapter 7: concludes with a summary of the findings of the experimental work carried out in the thesis and highlights future research directions.

1.2 Administrative and Organizational Aspects

1.2.1 PhD Supervision

The experimental work documented in this thesis was carried out under the supervision of Dr R. Vasant Kumar, Reader in Materials Science; Head of Materials Chemistry Group, at Department of Materials Science and Metallurgy, University of Cambridge; Fellow of the Institute of Materials, Minerals & Mining; Fellow of Trinity Hall

1.2.2 Research Laboratory, Collaborations and Contributions

The experimental work presented in this thesis were conducted at the following institutions:

- Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK

Materials synthesis; X-ray diffraction (XRD); Scanning electron microscope (SEM); Energy dispersive X-ray spectroscopy (EDS); Gas sorption isotherm and pore size distribution analysis; Transmission electron microscope (TEM); Thermal gravimetric analysis (TGA); Raman Spectroscopy; Electrochemical tests

- Cavendish Laboratory, University of Cambridge, Cambridge, UK

X-ray photoelectron spectroscopy (XPS)

- School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, China

Electrochemical tests; Density functional theory (DFT) theoretical calculation

Some of the experimental work were conducted in collaboration with many experts from different institutions. Specifically, TEM was carried out with the help of Dr. Xiaoyu Peng, Dr. Giorgio Divitini, and Dr. Cate Ducati, University of Cambridge; Electrochemical tests and DFT theoretical calculation were conducted with the help of Prof. Renjie Chen, Dr. Yusheng, Ye, Beijing Institute of Technology, Cheng-Yen Lao, Dr. Kai Xi. Dr. Xiong He, Dr. Hyun-Kyung Kim and Dr. Yingjun Liu, University of Cambridge.

Chapter 2 Literature Review

2.1 Lithium-Sulfur Batteries at a Glance

To meet the constantly rising energy demand of our modern lifestyles, building better batteries is essential^[7]. One of the important parameters for evaluating batteries' performance is specific energy, the amount of energy per unit mass. It continues to reach new highs from the previous 40 Wh kg⁻¹ value of lead-acid batteries to the current 250 Wh kg⁻¹ value of LIBs as shown in **Figure 2.1**^[8]. Chemists can theoretically enhance the value of specific energy by increasing the operational voltage and/or the amount of electrons transferred per unit molecular weight of redox active reactants^[9]. However, batteries have the potential of thermal runaway and even explosion at a voltage higher than ~5 V due to the decomposition of organic electrolytes^[10]. Relatively, it is much more reasonable to develop multi-electron reaction systems for high energy density batteries.

POWERING UP

Portable rechargeable batteries tend to hit an energy-storage-per-weight limit. Lithium-ion technology has gone through several phases and types, but is also expected to reach a ceiling soon.

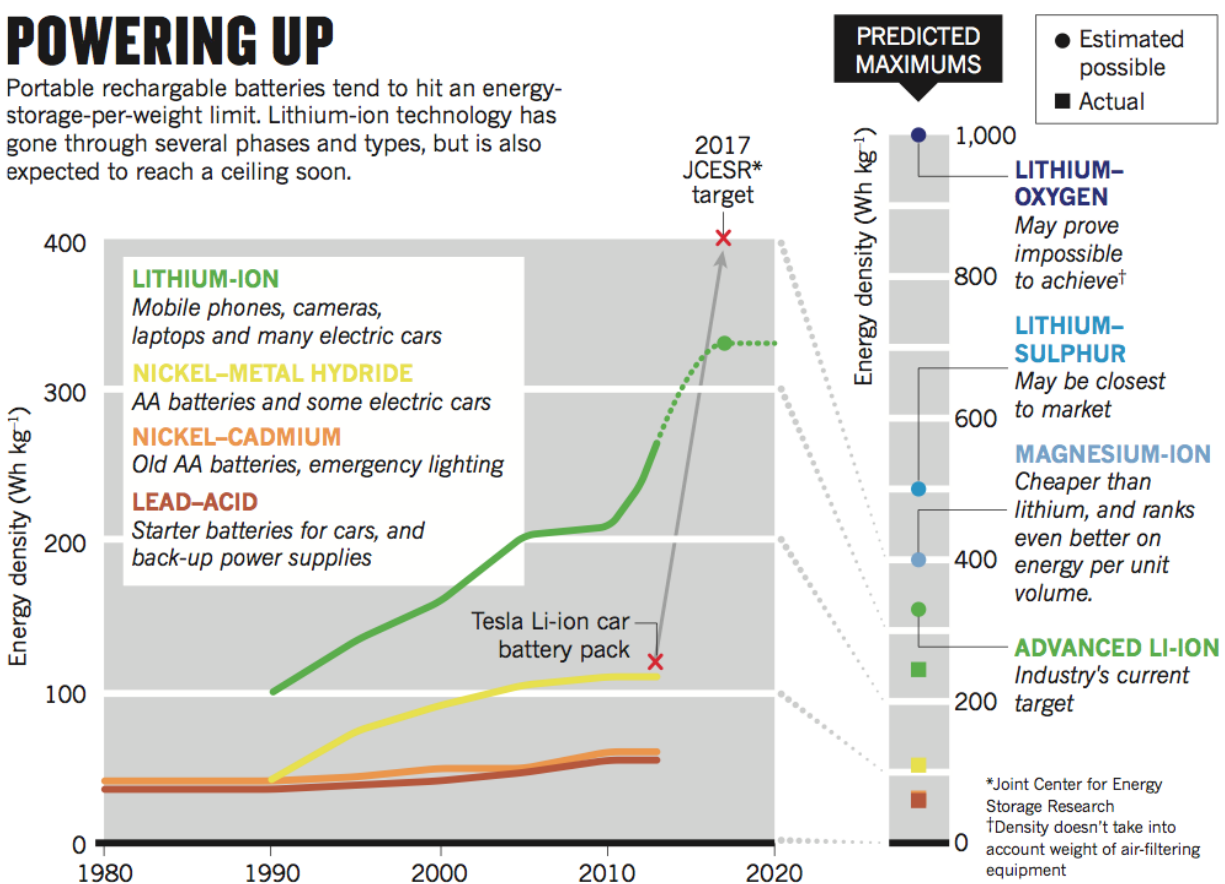


Figure 2.1: Evolution of Battery Energy Density over Years^[8].

As the third abundant element in earth's crust and the main byproduct of oil refinement, sulfur is a very attractive cathode material due to its low atomic number and the capability of transferring two electrons to form lithium sulfide (Li_2S) during conversion reaction with lithium^[11]. The research on Li-S batteries began ahead of LIBs' about half-century ago in 1962 when Herbert and Ullmann first proposed the concept of sulfur cathode^[12]. In the following two decades, intense research was carried out to investigate the electrochemical behavior of sulfur in various liquid organic electrolytes^[13-15]. It was found that the redox mechanism of sulfur was related to the electrolyte solvents and ether based systems had been proved to be the most efficient one for high performance because of their suitability for dissolving sulfur species^[16, 17]. Recently, ionic liquid and solid electrolyte have also been applied in Li-S batteries, giving consideration to their chemical stability^[18-20].

Another branch for advancing Li-S batteries is the development of sulfur scaffolds^[21] or functional interlayers^[22]. Nanostructured carbon materials have received much attention as sulfur hosts because of their large specific area, high pore volume and short path lengths for electronic and ion transport^[23]. Numerous carbon matrix with controlled morphology and porosity have been designed, including porous carbon^[24-28], carbon nanotubes^[29-33], graphene^[34-40], hollow carbon spheres^[41-46] and hybrid carbon^[47-50]. In addition, polymers^[51-57] and porous oxides^[58-63] have been used to modify carbon matrix or directly employed to host sulfur because of their strong ability in adsorbing polysulfides^[64]. Similar to the development trend of sulfur host, carbon materials^[65-69], polymers^[70, 71] and oxides^[72-74] are also the three main class of materials for designing interlayers, which are inserted between cathode and separator in order to mitigate the diffusion of polysulfides from cathode to lithium anode.

According to the statistics regarding the publications of Li-S batteries within recent 10 years, there is a slight increase in the number of publications from 2007 to 2010. After that, the number has risen exponentially and continues to do so until now (**Figure 2.2**). Undoubtedly, Li-S batteries currently represent an intense field of research. And it is expected that with efforts in engineering materials and understanding redox mechanism, Li-S batteries will surpass new horizons in the coming years and ultimately fuel the revolution in communication and transportation.

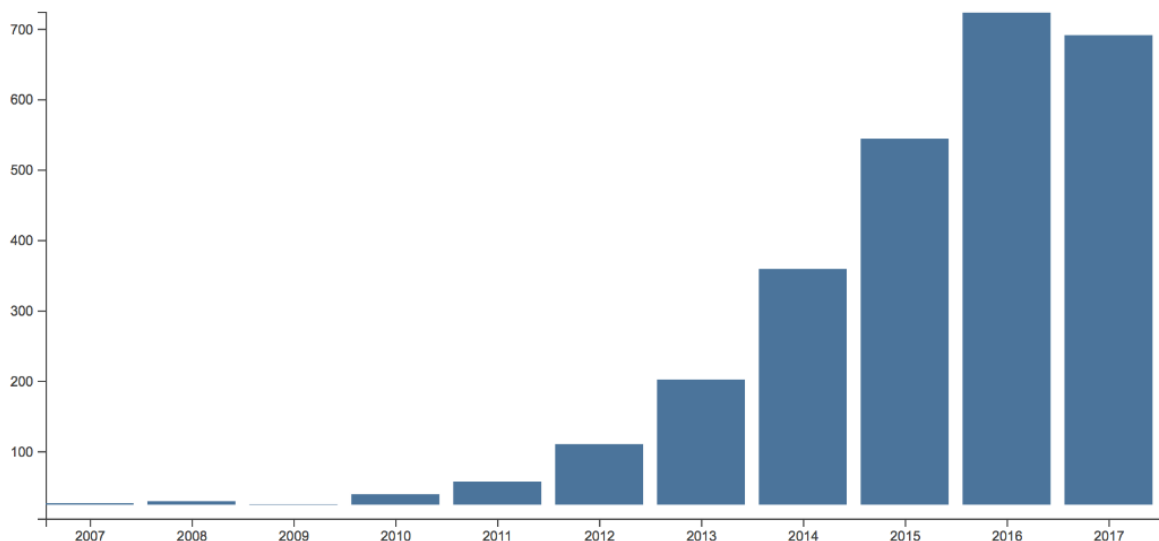


Figure 2.2: Statistics of Publications of Li-S Batteries in Recent Years (Web of Science, 2017 still in progress).

2.2 Electrochemistry

Typical Li-S batteries are composed of a sulfur cathode, a lithium anode and an electrolyte in between^[75]. This configuration was initially presented in 1960s and is still being used as the main platform for the fundamental research of sulfur chemistry. In principle, sulfur is reduced to form lithium sulfide at the cathode during discharge while lithium metal is oxidized at the anode^[76, 77]. The overall redox can be described by the reaction $\text{S}_8 + 16\text{Li} \leftrightarrow 8\text{Li}_2\text{S}$. This electrochemical reaction between sulfur and lithium is a non-topotactic assimilation process and involves two electrons transfer per sulfur atom. According to Faraday's Law, sulfur with an atomic number of 16 and a valence state of 2 in the most reduced state, offers a theoretical capacity of 1675 mAh g^{-1} , which is the highest among solid cathode materials^[78].

In fact, on the basis of previous experimental results, the mechanism of Li-S batteries is quite controversial. In general, the discharge process in ether-based liquid electrolytes can be divided into two stages, corresponding to the two plateau behavior of discharge curves^[79] (**Figure 2.3**). At a high and steep plateau around potential of 2.3V, cyclo- S_8 ring opens up and is reduced to long-chain polysulfides Li_2S_n ($4 < n < 8$) by combining with Li-ions. As discharge goes onward, the breaking of S-S bond continues and short-chain polysulfides Li_2S_n ($2 < n < 4$) are formed at a long and planar plateau around potential of 2.1V. At the end of discharge round the potential of 1.5 V, Li_2S is eventually produced. On charging, the reverse reaction can occur with the oxidation of Li_2S and the formation of elemental sulfur.

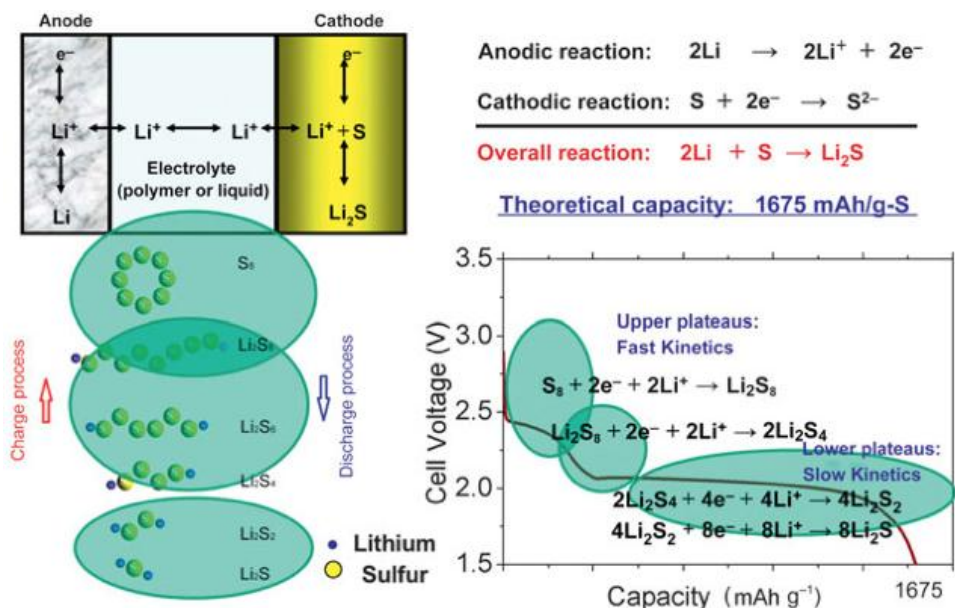


Figure 2.3: Illustration of the Multi-Step Electrochemical Mechanism Involved in a Typical Li-S Battery, Consisting of a S Cathode, Organic Electrolytes and a Li Anode.

On the other hand, some research indicated that the redox mechanism of Li-S batteries could be much more complicated due to the co-existence of several kinds of sulfide radicals and ions^[80-82]. To clarify the electrochemical reaction process, much effort has been made to identify and quantify those intermediate species by using advanced characterisation technologies^[83]. For example, using UV-visible absorption spectroscopy, high-performance liquid chromatography, and electron spin resonance spectroscopy, Barchasz and coworkers found that S_8^{2-} was initially formed at the first reduction stage and then disproportionated into S_6^{2-} , which was further reduced to S^{3-} radical and S_4^{2-} . After that, a sequence of short polysulfide compounds were formed at the second reduction stage, including S_3^{2-} , S_2^{2-} , S^{2-} ^[84]. According to in-situ XRD studies, the reduction of shorter sulfur species was not successive but rather simultaneous. Li_2S can be produced at the very beginning of the second reduction stage, although the kinetics is quite slow due to the solid-state diffusion^[85]. Recently, Nazar and coworkers monitored the species evolution over the entire redox range using operando X-ray absorption spectroscopy^[86]. It was found that S_6^{2-} was an important intermediate specie in both discharging and charging process. The fast reduction kinetics of S_6^{2-} can keep sulfur in reserve, which is the reason for the limited discharge capacity. Meanwhile, the maximum of S_6^{2-} in electrolyte coincided with the voltage rising during charging, which can be used to signal the final oxidation of S_6^{2-} to S_8 .

2.3 Technical Challenges

Undoubtedly, understanding the fundamental electrochemistry of sulfur is essential for solving the performance-related problems of Li-S batteries. The critical problem is the severe capacity decay caused by the dissolution and diffusion of polysulfides in organic electrolyte^[87, 88]. Specifically, long-chain polysulfides (Li_2S_x , $4 < x < 8$) can easily dissolve in organic solvents and diffuse to anode, where they can react with metal lithium to form short-chain polysulfides (Li_2S_x , $1 < x < 4$). Some of these species such as Li_2S or Li_2S_2 can deposit on the surface of lithium anode and cause irreversible loss of active material, others can diffuse back to the cathode and be re-oxidized, resulting in the notorious redox shuttle and low Coulombic efficiency. Another problem is the volume change of sulfur cathode during cycling because of the density difference between Li_2S (1.67 g cm^{-3}) and sulfur (2.03 g cm^{-3}). Theoretically, there is a volume expansion of $\sim 80\%$ during the whole discharge process, which can lead to cathode pulverization and thus capacity degradation from loss of ionic and electronic contacts^[89, 90]. Last but not least, the insulating nature of sulfur and Li_2S can inevitably lead poor electrochemical accessibility. Hence, making Li-S batteries practical is the Holy Grail in the development of next-generation energy storage systems.

2.4 A Nano Approach to Better Utilization of Sulfur Species

Nanomaterials with at least one dimension less than 100 nanometer, have received great attention for electrochemical storage because they have large area to volume ratio and exhibit better electric and mechanical properties than their bulk counterparts^[91-93]. More importantly, their small dimension ensures short diffusion path way and high interfacial kinetics, which are beneficial for high-power lithium/lithium-ion batteries^[94-96]. Until now, numerous nanostructured materials with controlled morphology and porosity have been prepared as hosts or interlayers for high-performance Li-S batteries, ranging from carbon, polymer to metal oxide. The detailed progress regarding this aspect will be elaborated in the following sections.

2.4.1 Cathodes

2.4.1.1 Carbon

Nano-structured carbon materials have been considered attractive matrices for hosting electrode materials due to their good conductivity, mechanical stability and lightweight^[23, 97, 98]. For Li-S batteries, sulfur can be easily introduced into the inner pores or surface of carbon by thermal infiltration or in-situ chemical deposition method^[99, 100]. The conductive carbon matrix, acting as an electrochemical chamber, can not only facilitate the electron transfer but also mitigate the dissolution of long-chain polysulfides. Furthermore, high sulfur loading can be achieved by tuning the porosity and morphology of carbon. An ideal design for carbon matrix should have the following features: (1) Large pore volume for high sulfur content; (2) Enough voids and robust frameworks for buffering the volume change of sulfur cathode during charging and discharging; (3) Closed structure for containing soluble polysulfides. (4) Good electrolyte accessibility.

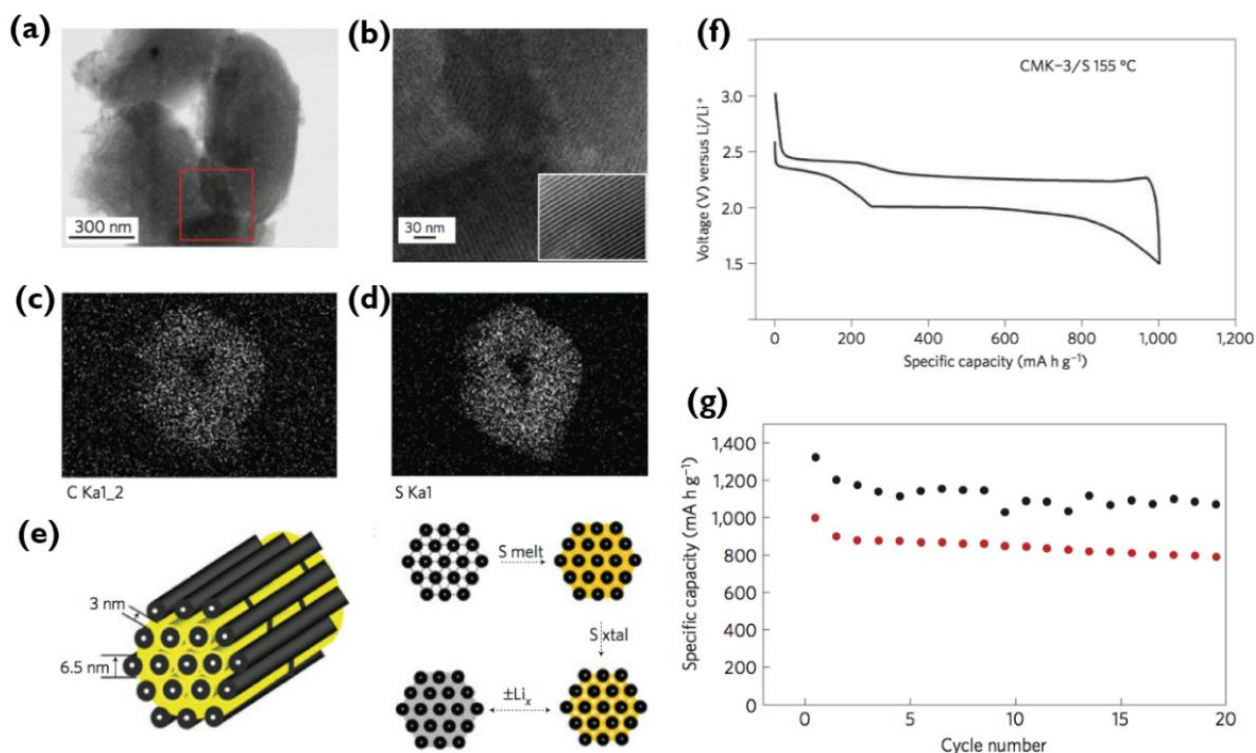


Figure 2.4: (a, b) TEM Images of S/OMC Composites with Different Magnification; (c, d) Elemental Mapping of C and S; (e) Schematic of S/OMC Composite; (f) Discharge-Charge Profile of S/OMC Composites; (g) Cycle-Performance Comparison Of OMC/S-PEG (Upper Points, In Black) Versus S/OMC (Lower Points, In Red) ^[101]

Over the last half decade, carbon materials with controlled pore structure have been prepared as sulfur hosts. Pore structure can be classified into three kinds by size, including macropore ($> 50\text{nm}$), mesopore ($2\text{-}50\text{ nm}$) and micropore ($<2\text{nm}$). Encapsulation of sulfur into highly ordered mesoporous carbon (OMC) was pioneered by Nazar's group in 2009^[101]. As shown in **Figure 2.4 (a-e)**, OMC was synthesized using a hard template method and consisted of arrays of hollow 6.5 nm nanorods with $3\text{--}4\text{ nm}$ channel void. It not only ensured intimate contact with sulfur but also allowed fast lithium ion diffusion. As a result, S/OMC composite with a sulfur loading of $70\text{ wt } \%$ delivered an initial capacity of 1005 mAh g^{-1} with a Coulombic efficiency of $99.94\text{ } \%$ (**Figure 2.4f**). Moreover, coating hydrophilic polyethylene-glycol (PEG) on S/OMC composite further enhanced the trapping of polar polysulfides, resulting in better capacity (**Figure 2.4g**).

To investigate the effect that the texture of mesoporous carbon has on the performance of Li-S batteries, Li and coworkers introduced sulfur into a series of mesoporous carbon with tunable pore sizes ($22, 12, 7, \text{ and } 3\text{ nm}$) and pore volumes (from 1.3 to $4.8\text{ cm}^3\text{ g}^{-1}$)^[102]. It was found that all samples had very similar initial capacity when sulfur loading was close to the maximum limit of pore volume. This suggested the performance of batteries were determined by the electrochemical accessibility of sulfur on the surface of pores. Interestingly, when sulfur was partially filled in the pore, much improvement in capacity retention was achieved, indicating that the unoccupied space within pores can enhance the trapping of polysulfides.

In addition to the pore volume, pore size distribution of carbon is also of key importance in terms of cycle stability and rate capability of batteries. For example, spherical carbon nanoparticles with mesopores of about 6.0 nm and 3.1 nm were fabricated using a two-step casting process^[103]. This bimodal mesoporosity contributed to a distinct pore volume of $2.63\text{ cm}^3\text{ g}^{-1}$ and a high specific surface area of $2445\text{ m}^2\text{ g}^{-1}$. Sulfur was introduced using a melt-diffusion method and preferentially filled in the smaller pores (3.1 nm). Meanwhile, electrolytes can penetrate through the larger pores (6 nm). Remarkably, as sulfur ratio was increased from 50 to 70% , the as-prepared sulfur-carbon composites exhibited comparable high capacity and good cycle life even at a relatively high current rate of 1C (1675 mA g^{-1}).

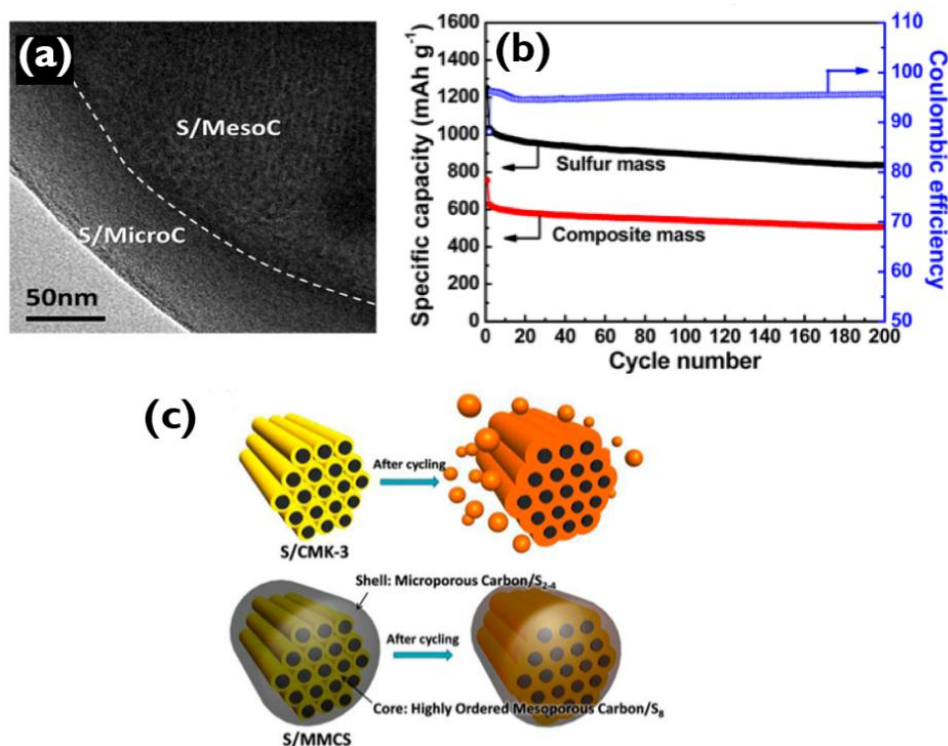


Figure 2.5: (a) TEM Image, (b) Cycle Performance and (c) Schematic of S/MMCS Composite^[105].

Hierarchical meso/micropore is another promising bimodal porosity for carbon materials. Liang and coworkers added microporosity (<2 nm) into the intrawalls of a mesoporous carbon (7.3 nm) by a chemical activation method^[104]. The micropores provided a high specific areas of 962.4 m² g⁻¹ and a pore volume of 0.503 cm³ g⁻¹ for housing sulfur while the mesopores facilitated lithium ion transfer. By taking advantages of the synergistic effect of the hybrid porous structure, the sulfur utilization was as high as 94.6% for initial cycle. However, obvious capacity decay occurred within 50 cycles, which is ascribed to the dissolution of polysulfides into electrolytes from the structure defects and deformity caused by the aggressive chemical etching. Recently, Li and co-workers reported the synthesis of a core-shell structured meso-microporous carbon (MMCS) by a nano casting method using SBA-15 as hard template and sucrose as carbon source^[105]. Both the mesoporous carbon core and microporous shell acted as sulfur host (**Figure 2.5a**). The composite maintained a reversible capacity of 837 mAh g⁻¹ with capacity retention of ~81% after 200 cycles at 0.5 C (**Figure 2.5b**). The core-shell structure of carbon host brought advantages in two aspects. First, the mesoporous carbon core with high pore volume and ordered conductive channel ensured high sulfur loading and utilization. Second, the microporous carbon shell with strong absorbing ability acted as a physical barrier to confine soluble polysulfides (**Figure 2.5c**).

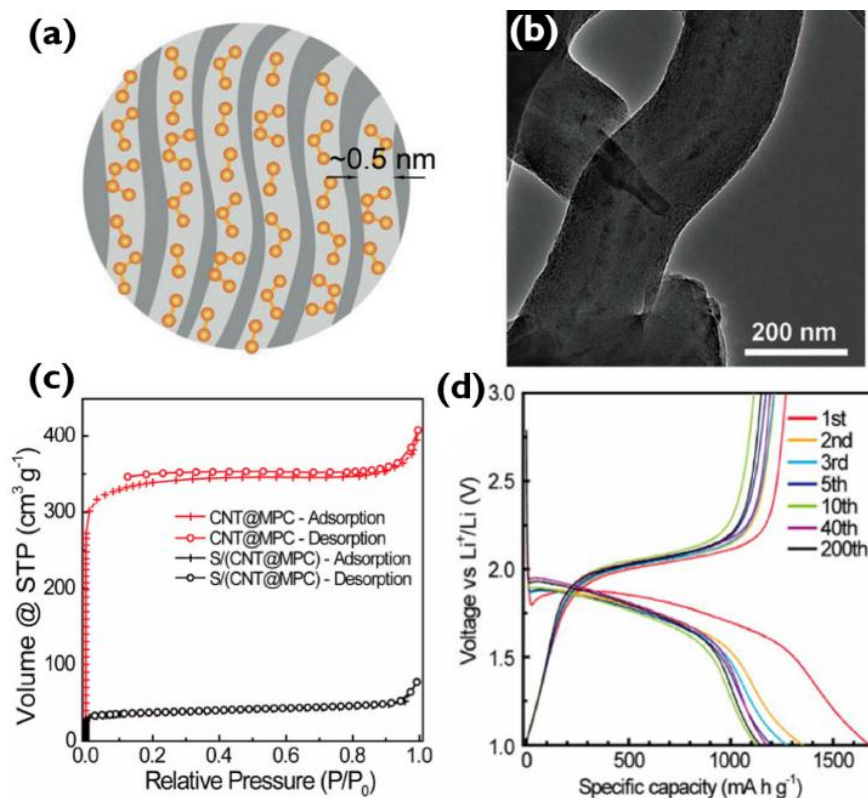


Figure 2.6: (a) Scheme of S Molecules Confined in Micropores; (b) TEM Image of S-CNT@MPC Composite; (c) N₂ Adsorption/Desorption Isotherms of S-CNT@MPC and CNT@MPC Composite; (d) Charge-Discharge Profile of S-CNT@MPC Composite at Different Cycles^[106].

The form of sulfur molecules also varies with the pore size of carbon matrix. Guo and coworkers found that only chain-like sulfur molecules like S₂ or S₄ can exist in micropores less than 0.5 nm due to the confined space(**Figure 2.6a**)^[106]. A coaxial structured carbon matrix with a carbon nanotube (CNT) core and a microporous carbon (MPC) sheath was prepared as sulfur host, which had a specific surface area of 936 m² g⁻¹ and a narrow pore size distribution of 0.5 nm (**Figure 2.6 b and 2.6c**). With a sulfur loading of ~40% wt in the micropores, the as-prepared S-CNT@MPC composite cathode had an impressive cycling stability. However, instead of a typical two plateau discharge behavior, the cathode only showed a single long output plateau at 1.9 V, which could be attributed to the direct reduction from short chain S₂₋₄ to S²⁻ (**Figure 2.6d**). To further give insight into the new redox mechanism, Huang and coworkers investigated the electrochemical response of S₂₋₄ confined in ordered microporous carbon^[107]. They proposed that the micropore of carbon can prevent the penetration of electrolyte solvents and ensured a solid-solid redox reaction, which retarded the lithiation of sulfur and resulted in lower discharge plateau. Confining sulfur in microporous carbon is an effective way to mitigate capacity degradation, but it cannot improve the specific energy of battery due to the limited sulfur loading and lithiation potential hysteresis. Hence, it is necessary to control the porosity of carbon matrix for high performance Li-S batteries.

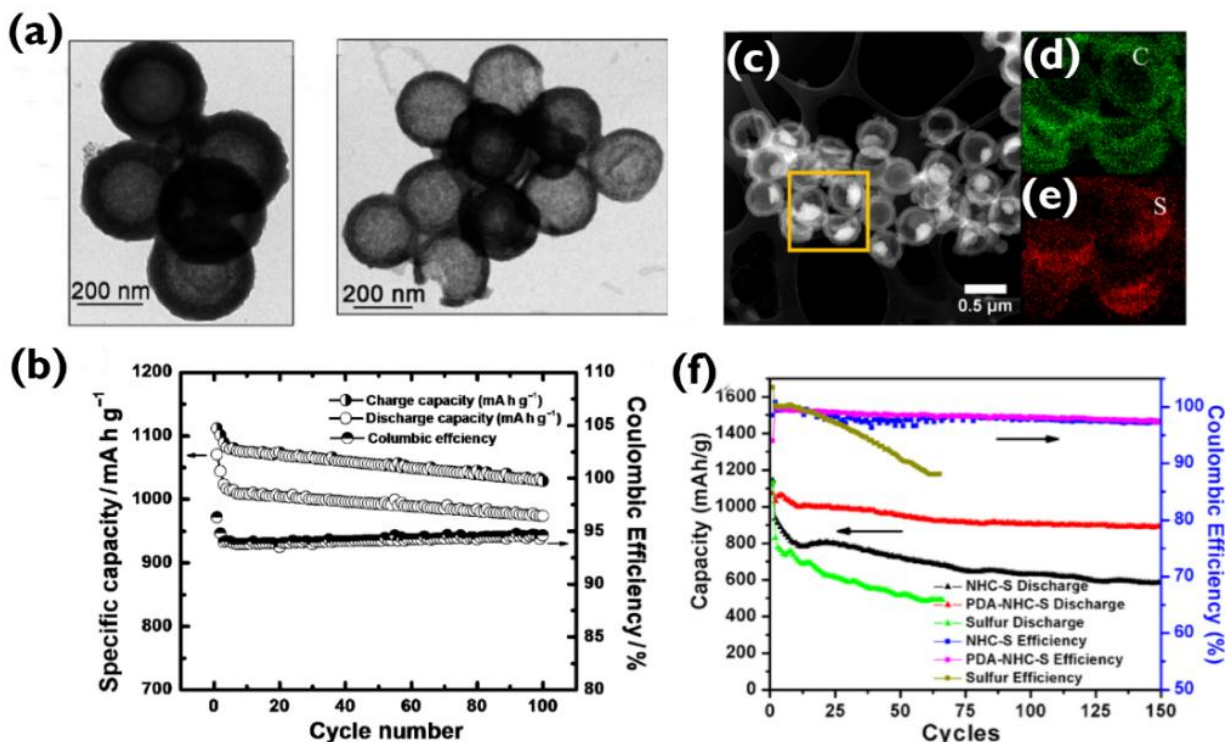


Figure 2.7: (a) TEM Images and (b) Cycle Life of S@C sphere Composites; (c) STEM Images of NHC-S Composite; (d-e) Elemental Mapping of C and S; (f) Cycle Performance^[109].

Very recently, hollow structured porous carbon has raised broad interest as sulfur host due to its large internal space. It not only provided sufficient room for accommodating sulfur but also offered a closed structure for confining polysulfides. Porous hollow carbon spheres with high specific surface area of 648 m² g⁻¹ and an average 3 nm pore diameter were synthesized by hydrolysis of a metal oxide templated carbon precursor^[108]. Sulfur was encapsulated into the internal void and porous shell through vapor infusion (**Figure 2.7a**). The composite with a sulfur loading of 70 wt% had an initial capacity of 1071 mAh g⁻¹ and exhibited an excellent cycle life with 91% capacity retention after 100 cycles (**Figure 2.7b**). Similarly, Zhou and coworkers embedded sulfur into nitrogen-doped hollow carbon spheres (NHC), which had a specific surface area of 1538 m² g⁻¹, a pore volume of 2.02 cm³ g⁻¹, and a primary pore size distribution at 3.2 nm (**Figure 2.7c-e**)^[109]. The NHC played multi-roles. First, it controls the size of the sulfur core. Small S particles are beneficial for high specific capacity and rate capability. Second, it facilitates the electron transfer from/to sulfur and thus improve the conductivity of sulfur cathode. In addition, the N-doping can enhance the adsorption of polysulfides through the coordination interaction between lithium polysulfides and nitrogen. Benefiting from the above characteristics, the NHC-S composite exhibited much improved capacity and cycle life than pure sulfur cathode (**Figure 2.7f**).

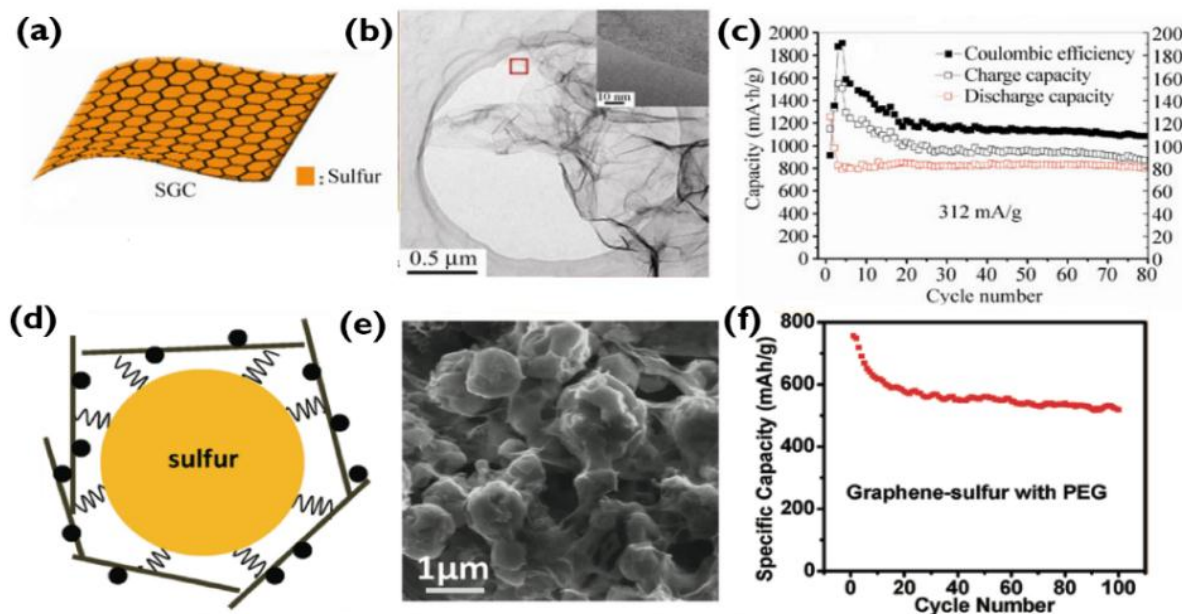


Figure 2.8: (a, d) Scheme of the composite structures; (b, e) TEM and SEM images; (c, f) Cycle performance of S/graphene and graphene-S/PEG Composites ^[116,117].

Graphene, a two-dimensional (2D) and one-atom-thick carbon layer, is the basic building block of all graphitic materials ranging from 0D fullerenes, 1D nanotubes to 3D graphite^[110]. It was first isolated by manual mechanical cleavage of graphite using a scotch tape and has opened up new applications in the field of energy storage due to its excellent electrical conductivity, high surface area and mechanical flexibility^[111-115]. Recently, chemically reduced graphene oxide has been employed to hold sulfur due to its facile synthesis procedure. For example, Sun and coworkers developed a one-pot wet chemical method to simultaneously reduce graphene oxide and introduce sulfur into its interlayer galleries (**Figure 2.8a and 2.8b**)^[116]. Because of the homogeneous dispersion of sulfur in the graphene, a reversible capacity of 804 mAh g⁻¹ was achieved after 80 cycles, corresponding to a capacity retention of 63.4% (**Figure 2.8c**). Although sulfur utilization was much improved due to the fast electron transfer network of graphene, capacity degradation was still observed because the hydrophobic graphene cannot effectively trap polar polysulfides. Modifying graphene/sulfur cathodes by hydrophilic polymers is a valid approach to enhance the confinement of polysulfides. Graphene wrapped S/PEG composites were synthesized using a solution assembly method^[117]. As shown in **Figure 2.8d and 2.8e**, the PEG coating layer can not only serve as a capping agent to limit the particle size of sulfur but also act as a cushion to buffer the strain arising from the volume change of sulfur cathode during cycling. More importantly, it provided a chemical gradient to retard the diffusion of polysulfides. As a result, the composite exhibited 87% capacity retention of its initial capacity over more than 100 cycles (**Figure 2.8f**).

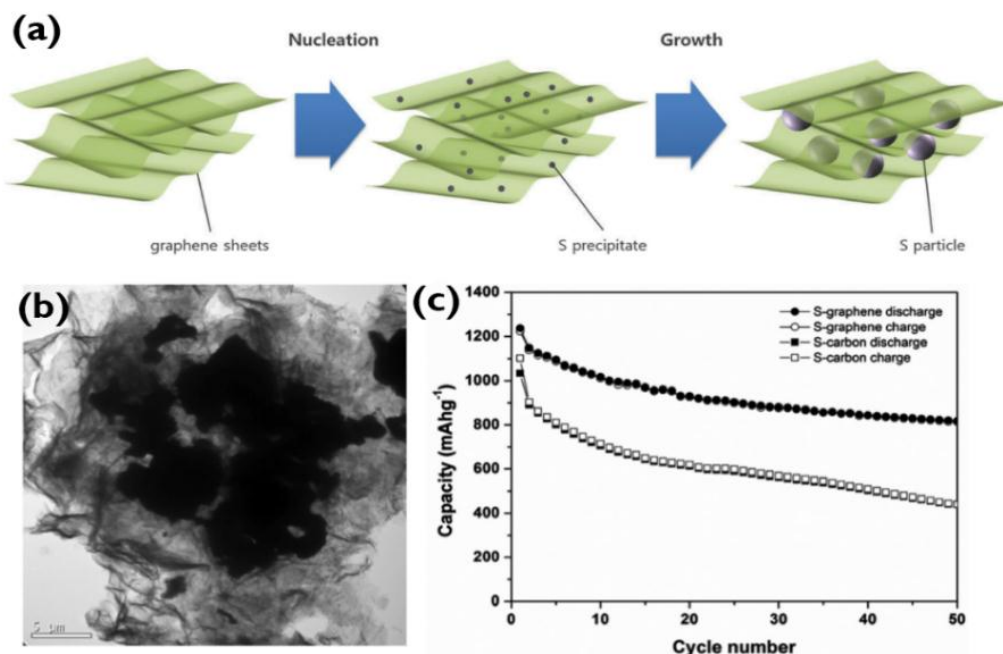


Figure 2.9: (a) Schematic of a Heterogeneous Crystal Growth Mechanism of S particles on HF-treated Graphene; (b) TEM Image of S/HF-Treated Graphene Composite; (c) Cycle Performance^[119].

The porosity and morphology of graphene are also key aspects that affect the performance of Li-S batteries. Through chemical activation, Ding and coworkers introduced dense nanopores on the surface of graphene, which can be used as micro-reactors for constraining polysulfides and accommodating the change in volume of the sulfur cathode during cycling^[118]. The specific area and pore size distribution of porous graphene can be controlled by adjusting the mass ratio of potassium hydroxide to graphene. When the ratio was 10:1, the activated graphene had a suitable specific area of 1616 m² g⁻¹ and an average pore size of 3.8 nm. Sulfur was melted by heat treatment and driven into these nanopores by capillary force. The composite with a sulfur loading of 67 wt% delivered an initial capacity of 927 mAh g⁻¹ at a current rate of 1C and had a capacity retention of 74% after 100 cycles. In addition, Park and coworkers proved that hydrogen fluoride (HF) treated graphene can afford active nanopores for controlling the nucleation of sulfur in an aqueous solution^[119]. According to a heterogeneous crystal growth mechanism, sulfur seeds with critical radii were first precipitated on these sites and then grew up to a few microns in size at optimized concentration and reaction time (**Figure 2.9a**). Meanwhile, the flexible graphene can wrap around the grown sulfur particles to ensure good electrical conduction and confinement of polysulfides during cycling (**Figure 2.9b**). The composite with a sulfur content of 83 wt% exhibited a capacity of 1237 mAh g⁻¹ at the initial discharge and a capacity retention of 67% after 50 cycles (**Figure 2.9c**).

Recently, graphene with tailored morphologies has also been developed for containing sulfur. For example, Wang and coworkers used an oil–water system to fabricate saccule-like sulfur–graphene composites^[120]. Sulfur particle sizes with ranging from 10 to 100 nm were encapsulated in the interior of graphene capsule due to the small droplets of oil. Compared with the conventional 2D structure, saccule-like structure of graphene can prevent the contact of sulfur with electrolytes and is more effective to restrict polysulfides. In addition, it can also provide sufficient room to accommodate stress arising from the volumetric change of sulfur cathode during cycling. All these merits contributed to a reversible capacity of 621.9 mAh g⁻¹ after 60 cycle with capacity retention of 85.8% at a current rate of 1C.

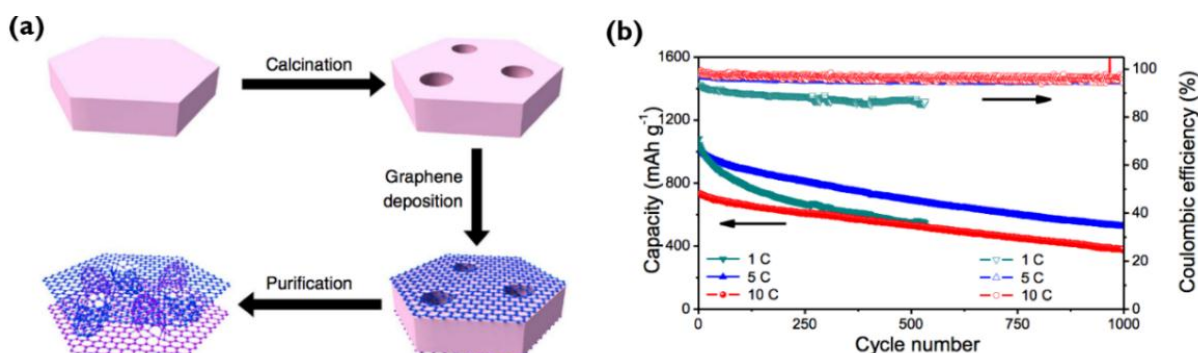


Figure 2.10: (a) Scheme for the Synthesis of Unstacked DTG; (b) Cycle-Performance of S-DTG at Different Rates^[121].

2D graphene also tends to irreversibly restack due to the π - π interaction, resulting in reduced surface area and poor energy storage performance. To solve this problem, Zhao and coworkers used chemical vapor deposition method to fabricate an unstacked double-layer templated graphene (DTG) with intrinsic protuberances (**Figure 2.10a**)^[121]. Owing to the high conductivity, mesoporous structure and large surface area of DTG, the obtained S-DTG composite maintained a capacity of 380 mAh g⁻¹ at an ultrahigh current density of 10C after 1000 cycles (**Figure 2.10b**). To combine the benefits of hollow structure and the excellent properties of graphene, Peng and coworkers developed a mesoscale approach to hollow graphene nano shells (HGNs)^[122]. The specific area and pore volume of the obtained HGNs were 979 m² g⁻¹ and 1.98 m³ g⁻¹, respectively. The large hollow interior can accommodate sulfur and its volume variation during charge-discharge process while the interconnected few layer graphene shell can offer good electron/ion accessibility. Even at a current rate of 1C, the cathode reached an initial capacity of 1098 mAh g⁻¹ and retained a capacity of 419 mAh g⁻¹ after 1000 cycles.

Carbon nanotubes (CNTs) are tubular cylinders of one or multi-layer graphene^[123]. Considering their good mechanical and electrical properties, CNTs are favorable conductive matrix for sulfur. Manthiram and coworkers developed a self-weaving sulfur/multi-wall carbon nanotube (MWCNT) film via a facile vacuum filtration method (**Figure 2.11**)^[124]. The intertwined MWCNTs can provide cross-linked electrical and ionic pathways for facilitating fast charge/discharge. Besides, its tensile skeleton, serving as electrochemical reaction sites, can not only retain the integrity of cathode but also have good electrolyte-absorption ability. Without any additional polymer binder, conductive additives, or a separate metal current collector, the flexible S/MWCNTs film electrode exhibited a high capacity of 1352 and 1012 mAh g⁻¹ at a current rate 1C and 4C, respectively.

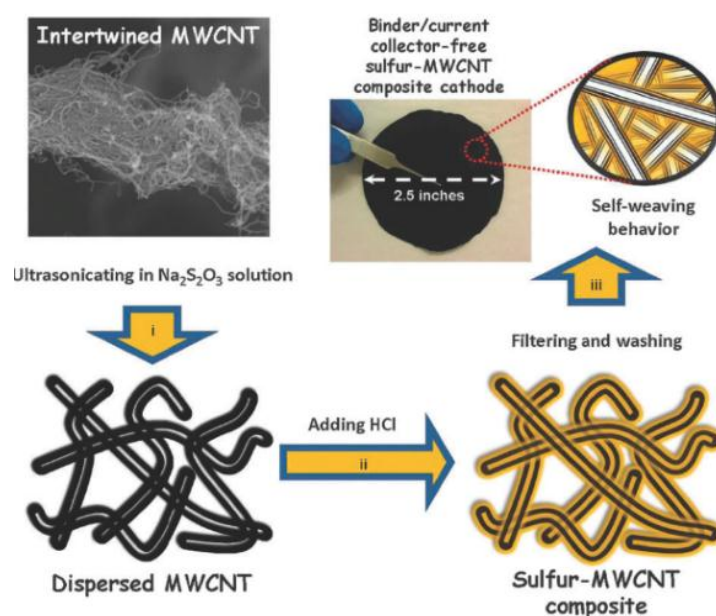


Figure 2.11: Schematic for the Preparation of Self-Weaving S/MWCNT Cathode^[124].

Based on the same concept, a flexible, binder-free CNT/S composite was prepared by template-directed chemical vapor deposition of CNT, followed by carbothermal reduction of sulfate^[125]. The CNT matrix with mesoporous wall provided conductive support and strong confinement for sulfur and polysulfides. As a result, the cathode with a sulfur loading of 23% wt delivered a capacity of 712 mAh g⁻¹ at a high current density of 6 A g⁻¹. Recently, Sun and coworkers developed a facile solution method to anchor sulfur nanocrystals on aligned CNT^[126]. The highly conductive, aligned CNT matrix can not only facilitate the transfer of electron and penetration of electrolytes but also provide adhesion points for confining polysulfides. Moreover, nano-sized sulfur particles can shorten the Li-ion diffusion path. When evaluated as cathode, the nano S-CNT composite delivered an initial capacity of 1071 mAh g⁻¹ and exhibited a long cycle life for 100 cycles with capacity retention of 85% at a current rate of 1C.

Another remarkable feature of CNTs is their ability to self-assemble hierarchical architectures. A S/MWCNT nano/microsphere was prepared by a simple ball-milling treatment^[127]. Because of their capability in offering fast electron and ion transport pathway and buffering volume change, the 3D MWCNT frameworks as sulfur host ensured a high capacity of batteries with good cycle retention. In addition, the hollow structure of this framework can effectively absorb electrolytes, resulting in good rate performance (**Figure 2.12**). As a result, a reversible capacity of 1000 mAh g⁻¹ was achieved after 100 cycles at 0.3 A g⁻¹.

Although self-woven CNTs provide robust and cross-linked conductive networks, their 1D morphology inherently limits the ion and electron transfer pathways along the long axis of the CNTs, which results in a low rate performance for the cell. Additionally, the surface areas and pore volumes of CNTs are much lower than those of porous carbon or graphene, resulting in limited sulfur loading and low interface kinetic activity. Hence, it is necessary to combine CNTs with other conductive matrices to overcome these problems by synergistic effects.

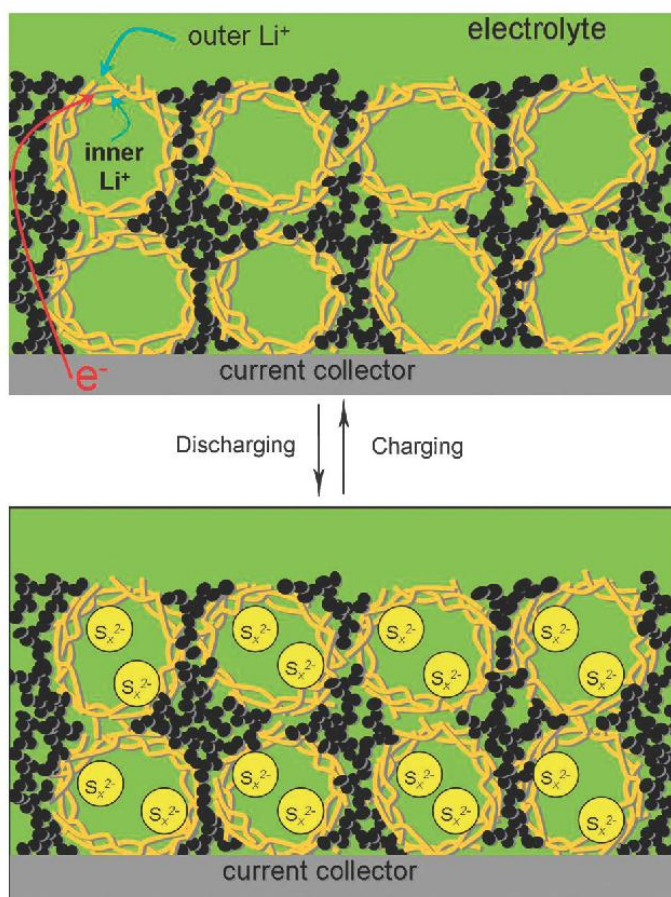


Figure 2.12: Model of the Discharge–Charge Process of S/MWCNT Nano/Microsphere with Hierarchical Architecture^[127].

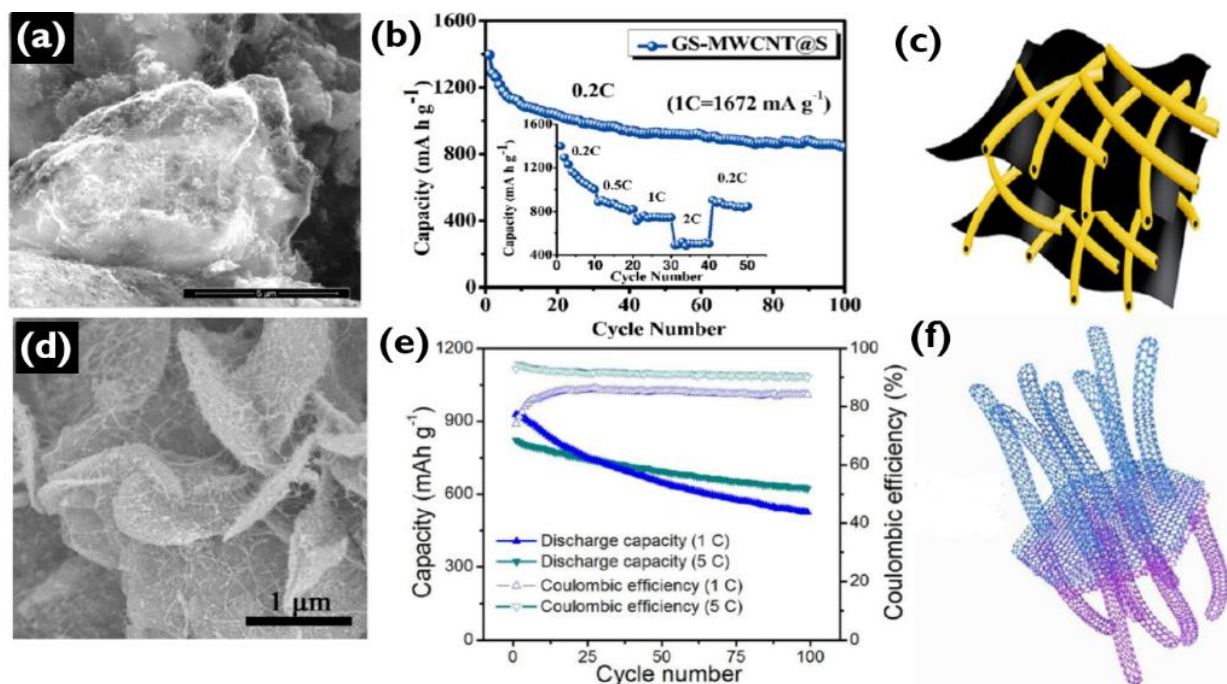


Figure 2.13: (a,d) SEM images; (b,e) Electrochemical Performance; (c,f) Structural Scheme of Sandwich Structured G-MWCNT@S and S-G/SWCNT/Composite^[128].

Recently, various kind of hybrid carbon have been prepared as sulfur hosts to tackle the intrinsic problems associated with sulfur chemistry. Among them, hierarchical graphene/CNTs is one of the most attractive candidates, considering their bridged 3D conductive networks and porous structure. Chen and coworkers embedded a core-shell structured MWCNT@S composites into the interlayer galleries of graphene (G) via a facile solution assembly process (**Figure 2.13a and 2.13c**)^[128]. The unique 3D sandwich-type architecture of the G-MWCNT@S composite brought advantages in electron/ ion transfer, the confinement of polysulfides and the accommodation of volume variation. Specifically, the hybrid carbon matrix consisting of MWCNT and graphene provided a 3D conductive network and effectively reduced the electron transfer resistance. The pores within this framework were favorable for fast ion diffusion. More importantly, the residual oxygen groups on the surface of the GS and the absorbent ability of the MWCNT generated synergistic effects in retarding the polysulfides dissolution. Finally, the flexibility of the graphene could buffer the volume change of the sulfur during cycling and prevent cathode pulverization. As a result, the G-MWCNT@S composite with a sulfur loading of 70 wt% maintained a reversible capacity of 844 mAh g⁻¹ after 100 cycles and also had a good rate performance of 743 mAh g⁻¹ at a current rate of 1 C (**Figure 2.13b**).

Similarly, sulfur was encapsulated into the internal of graphene/single-walled carbon nanotube (G/SWCNT) hybrids prepared by a catalytic growth method (**Figure 2.13d and 2.13f**)^[129]. Compared with physical combination, the chemical link between the SWCNTs and the graphene offered a higher electrical conductive pathway, thus achieving a higher sulfur utilization. In addition, the abundant mesopores and robust structure of G/SMWCNT afforded better confinement of polysulfides and accommodation of volume change of sulfur cathode. Accordingly, the S-G/SWCNT cathode with a sulfur loading of 60 wt% maintained a capacity of 650 mAh g⁻¹ after 100 cycles at 5 C with a Coulombic efficiency of 92% (**Figure 2.13e**).

CNT/porous carbon is also a promising combination that inherits both high conductivity and large specific area. Zhao and coworkers encapsulated MWCNTs into the hollow porous carbon nanotubes through a step by step method^[130]. With a large specific area of 822.8 m² g⁻¹ and a total pore volume of 1.77 m³ g⁻¹, the obtained tube-in-tube nanostructure was used as a sulfur host. The inner MWCNTs core can offer high conductivity to facilitate the transportation of both ions and electrons while the outer carbon layers can afford abundant micro/mesopores to mitigate the migration of polysulfides. Moreover, the void space between MWCNT and carbon layers can relieve the volume changes of sulfur upon cycling and keep the structure stable. These appealing features led to a reversible capacity of 647 mAh g⁻¹ at 2 A g⁻¹ after 200 cycles.

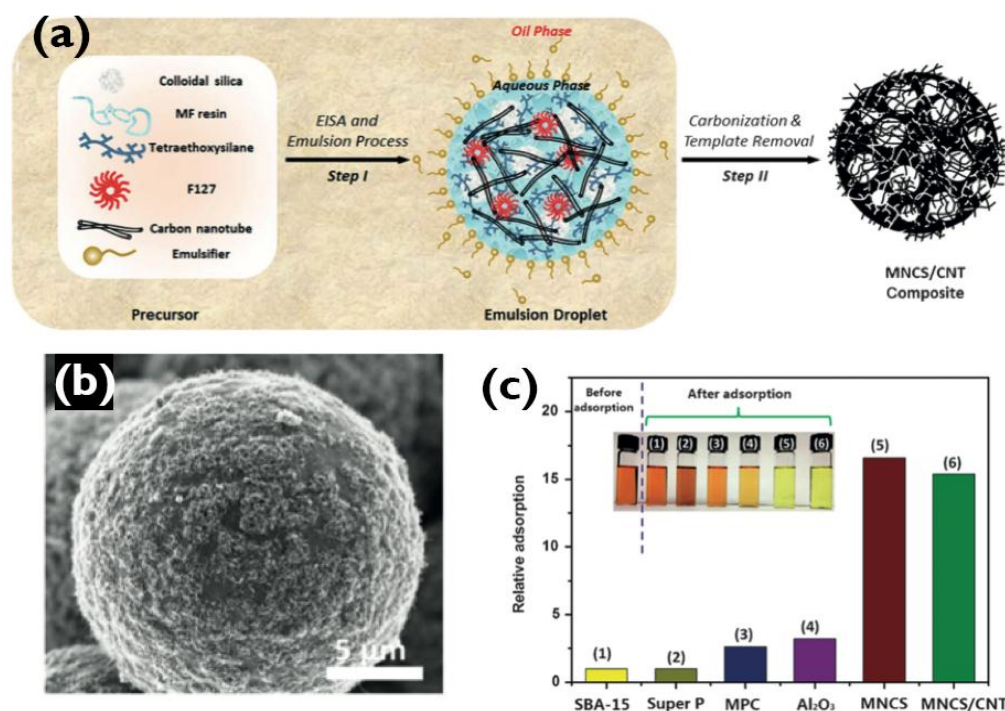


Figure 2.14: (a) Schematic Illustration of the Fabrication of MNCS/CNT Composite; (b) SEM Image of MNCS/CNT Composite; (c) Comparison of the Ability of Various Adsorbents in Absorbing Polysulfides^[131].

Another hybridization of CNT/porous carbon has been achieved by the interpenetration CNT into mesoporous nitrogen-doped carbon spheres (MNCS) using an evaporation-induced self-assembly method (**Figure 2.14a**)^[131]. The hybrid carbon composite had a microspherical morphology and a specific surface area of $615.02 \text{ m}^2 \text{ g}^{-1}$ (**Figure 2.14b**). Compared with mesoporous carbon and metal oxides, the hybrid MNCS/CNT had a much stronger adsorption behavior for polysulfides because of the chemical interaction between lithium ions in polysulfides and nitrogen functional groups in the MNCS/CNT framework (**Figure 2.14c**). As a result, the cathode with a sulfur content of 70 wt % delivered an initial specific capacity of 1480 mAh g^{-1} and had 90% retention over 200 cycles.

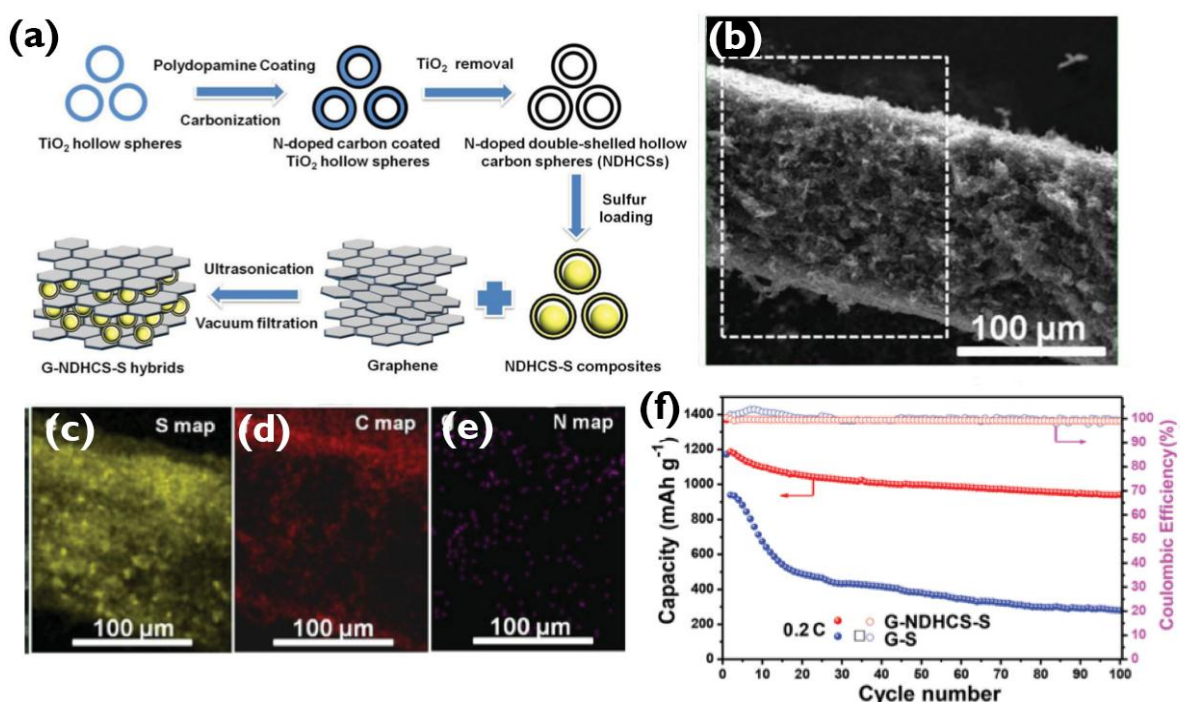


Figure 2.15: (a) Schematic Illustration of the Fabrication of the NDHCS-S Composite and G-NDHCS-S Hybrid Paper; (b) Cross-Section SEM Image of G-NDHCS-S Hybrid Composite; The Corresponding Elemental Mapping of S (c), C (d) And N (e); (f) Cycling Performance and Coulombic Efficiency of The G-NDHCS-S And G-S Electrodes^[50].

Finally, sulfur cathodes based on the assembly of graphene and porous carbon also exhibited superior electrochemical performance. Zhou and coworkers used a template-direct method to confine sulfur in N-doped double shelled hollow carbon spheres (NDHCSs), followed by graphene (G) wrapping (**Figure 2.15 a-e**)^[50]. The porous double shell and hollow structure of NDHCSs can offer sufficient space to accommodate sulfur and its volume change during cycling while the N-doping can benefit the immobilization of polysulfides by increasing their affinity/interaction with

carbon. Besides, the flexible wrapped graphene acted as conductive support and eliminated the need of binder and collector. Hence, the free-standing dual-confined sulfur cathode (G–NDHCS–S) with a sulfur loading of 62 wt% showed a high initial discharge capacity of 1360 mAh g⁻¹ at a current rate of C/5 and capacity retention of 69.1% after 100 cycles (**Figure 2.15f**). In addition, dual protection of sulfur cathode by carbon nanospheres (CSs) and graphene was reported^[132]. CSs played the role in carrying sulfur into the interlayers of graphene (G), which in return contributed to direct coverage of sulfur to inhibit the migration of polysulfides. In this way, the hybrid G-CS@S cathode exhibited an advantage over bare CS@S composite and maintained a reversible capacity of 815 mAh g⁻¹ after 100 cycles.

2.4.1.2 Metal oxides

Nano structured metal oxides are another kind of functional materials that have been used as hosts, additives, surface coating for sulfur cathodes. Because of the polarized surface induced by oxygen atoms, they have strong chemical interaction with polysulfide anions^[62]. In addition, they have suitable specific surface area and porous structure, which are favor for adsorption of polysulfides. Although the conductivity of metal oxides is low compared with carbon, it can be improved by introducing oxygen vacancy or conductive components. Various hybrid metal oxide/carbon matrices have been developed. Technically, fabrication of metal oxides based sulfur cathode is a valid approach to solve the problems plagued with Li-S batteries.

Initially, metal oxides were used as additives to retain polysulfides by on-site adsorption. For example, nano-sized manganese nickel oxide (Mg_{0.6}Ni_{0.4}O) particles were added to a sulfur/carbon black composite cathode^[133]. The addition of Mg_{0.6}Ni_{0.4}O particles with a diameter of 30-50 nm to the cathode provided new boundaries for charge transfer and significantly reduced the internal charge resistance. In addition, it was found that Mg_{0.6}Ni_{0.4}O particles effectively trapped polysulfides and catalyzed their reduction, leading to enhanced capacity and cycle stability. Similar effects were observed when Mg_{0.6}Ni_{0.4}O particles were introduced into a polyacrylonitrile (PAN)-S composite^[134]. The cathode with Mg_{0.6}Ni_{0.4}O loading of 4 wt% had a discharge capacity of 887, 710 and 445 mAh g⁻¹ at 0.5, 0.7 and 1 C, respectively.

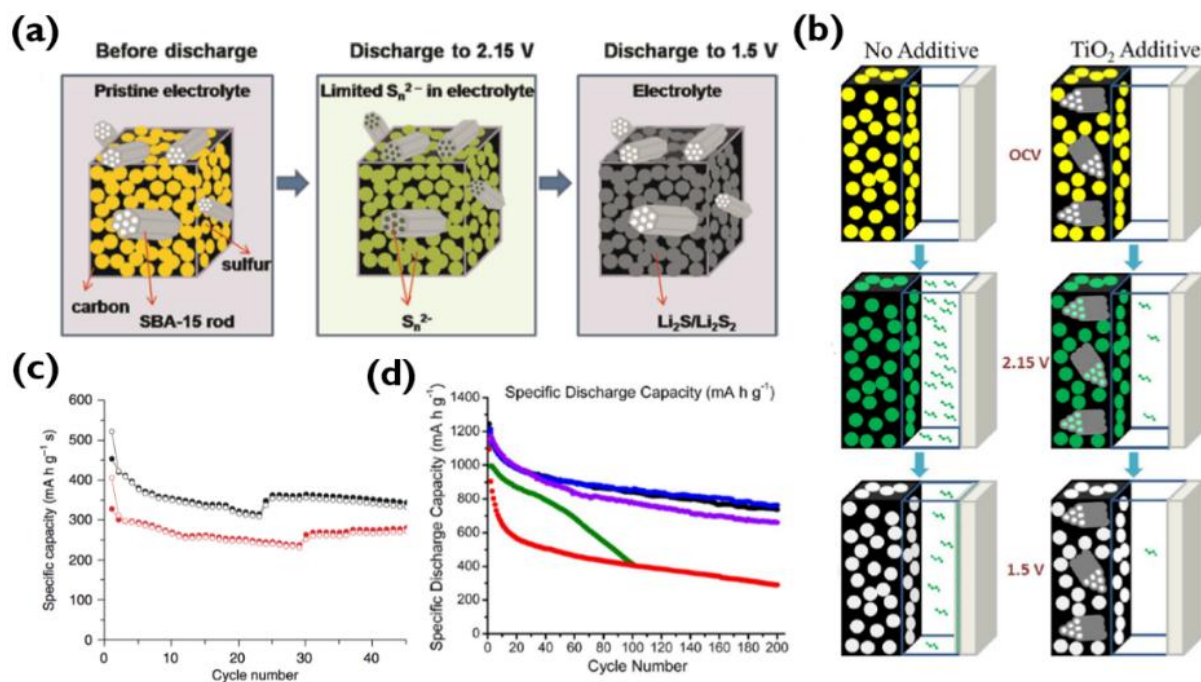


Figure 2.16: (a,b) Schematic of the Concept of the ‘Polysulfide Reservoir’ Afforded by SBA-15 and TiO_2 Embedded in S/C Composite; (c,d) Effect of SBA-15 and TiO_2 Incorporation on the Cycle Performance of S/OMC Cathode^[135].

Porous silica is another promising polysulfides absorbing agent. Inspired by a drug delivery system, Nazar and coworkers used triblock copolymer-templated SBA-15 as polysulfide reservoirs and placed them on the surface a OMC/S composite cathode, as shown in **Figure 2.16a**^[135]. Because of its high surface area and hydrophilic nature, SBA-15 had a physical interaction with polysulfides by surface adsorption. Besides, the positively charged silica surface can also assist polysulfides trapping via a weak binding. The adsorbed polysulfides by SBA-15 can also be released based on a diffusion-controlled mechanism. As a result, 94% of sulfur was reversibly adsorbed/desorbed by SBA-15 and participated in the electrochemical reactions even at the 40th cycle (**Figure 2.16c**). In fact, metal oxides with small particle size, porous structure, and high specific surface area are all potential candidates. For example, Nazar and coworkers further utilized mesoporous titania (TiO_2) as polysulfides sorbent for a sulfur/mesoporous carbon composite, which is more commercially viable and electroactive than SBA-15^[136]. Based on a similar adsorption/absorption mechanism, majority of polysulfides were trapped by the porous structure of TiO_2 . The addition TiO_2 to cathodes led to a 37% increase in capacity retention after 100 cycles (**Figure 2.16b and 2.16d**).

Metal oxide coating on sulfur cathodes can also inhibit the dissolution of polysulfides. OMC–S composite was enshrouded with a thin oxide layer via a surface-initiated growth method^[137]. Being poor electronic conductor, metal oxide can prevent the reduction of polysulfide to form insoluble Li_2S on the surface of cathode, reducing the irreversible loss of active material. Besides, they can enhance the structural stability of the sulfur cathode and act as physical barrier to block polysulfides diffusion, improving cycle stability. With optimized coating thickness, a capacity up to 600 mAh g^{-1} was achieved after 200 cycles. To avoid polarization arising from thick metal oxide coating, ultra-thin aluminum oxide (Al_2O_3) film was conformably grown on the surface of a sulfur/activated carbon cloth composite using a plasma-enhanced atomic layer deposition method^[138]. With a coating thickness less than 5 nm, the amount of sulfur confined in the cathode after 300 cycles was increased by 20%.

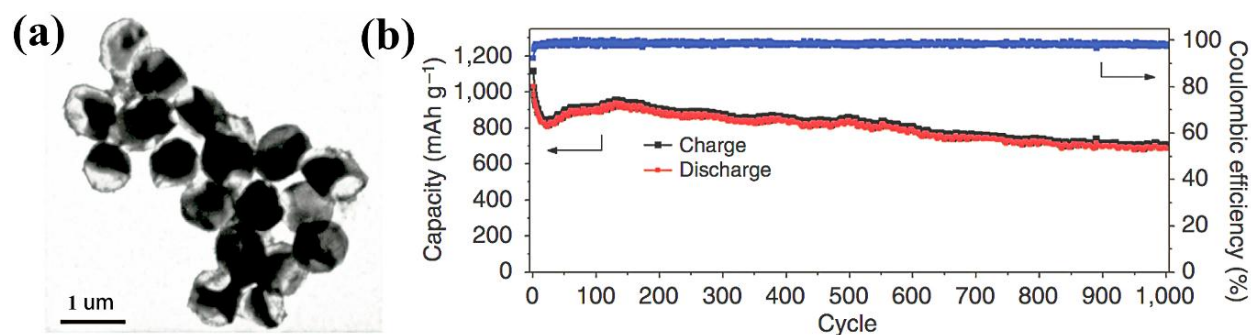


Figure 2.17: (a) Schematic of the Formation Process; (b) TEM Images; (c) The Particle Size Distributions; (d) Electrochemical Performance of Yolk-shell S@TiO₂ Composite ^[139].

In addition to precisely controlling coating thickness, keeping metal oxide coating shell intact is important to effectively limit polysulfides dissolution. Cui and coworkers coated mesoporous TiO₂ on mono-dispersed sulfur nanoparticles by hydrolysis^[139]. To prevent the crack of TiO₂ shell caused by the large volume expansion of sulfur core during cycling, a fraction of sulfur was leached using organic solvent and a yolk-shell structure was formed (**Figure 2.17a**). The capacity decay of the as-prepared composite over 1000 cycles was as small as 0.033% per cycle, which was much lower than that of its core-shell counterpart (**Figure 2.17b**). Clearly, the internal void played a key role in keeping the structural integrity of TiO₂ coating shell, which successfully mitigated the dissolution of polysulfides and enhanced cycle stability.

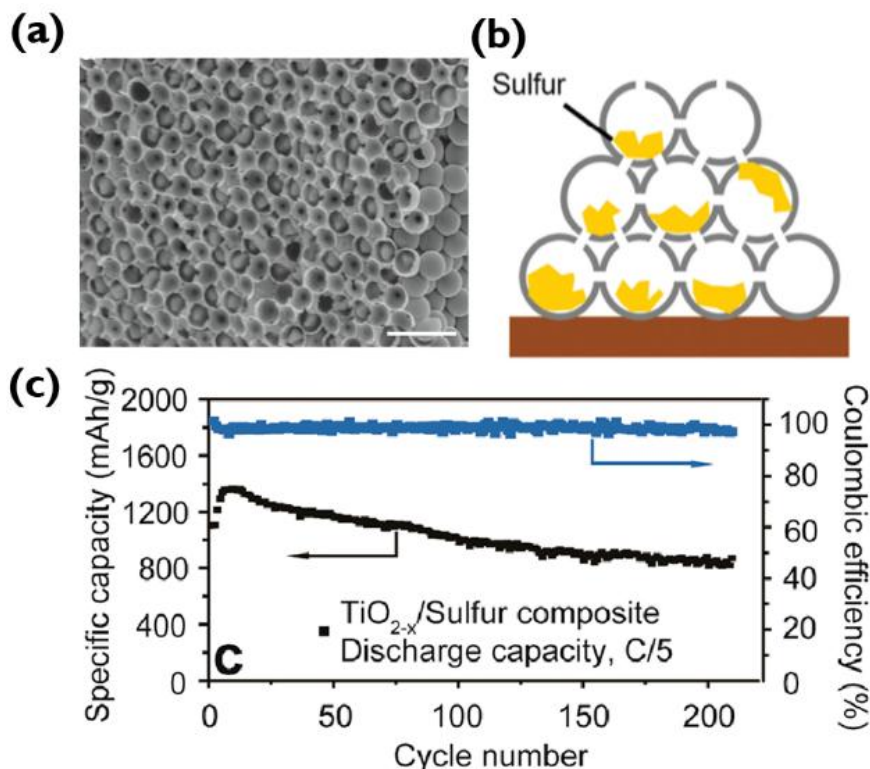


Figure 2.18: (a) SEM and (b) Schematic of TiO_{2-x} Inverse Opal after S Infusion; (c) Electrochemical Performance of TiO_{2-x}/S Composite^[140].

Metal oxides with tailored nanostructure and composition have also been demonstrated to be promising sulfur carriers because of their good conductivity and strong confinement of sulfur as well as polysulfides. For example, hydrogen reduced TiO_{2-x} with a 3D inverse opal structure was used as a free-standing matrix for hosting sulfur (**Figure 2.18a and 2.18b**)^[140]. The open channels within the framework afforded access to sulfur infiltration while the oxygen vacancies generated during reduction process can increase the conductivity of cathode and facilitate the utilization of sulfur. More important, the chemical interaction between TiO_{2-x} and S (S-Ti-O) can improve the surface adsorption of polysulfides. All these contributed to a reversible capacity of $\sim 890 \text{ mAh g}^{-1}$ after 200 cycles at a C/5 rate (**Figure 2.18c**). In addition, it was found that Magnéli phase Ti_nO_{2n-1} with a narrow band gap had a strong binding with sulfur species due to its abundant low coordinated Ti sites on surface^[141]. By taking advantages of the metallic conductivity and sulfur species binding ability of Ti_nO_{2n-1}, S/ Ti_nO_{2n-1} composite exhibited satisfactory capacity and cycle stability.

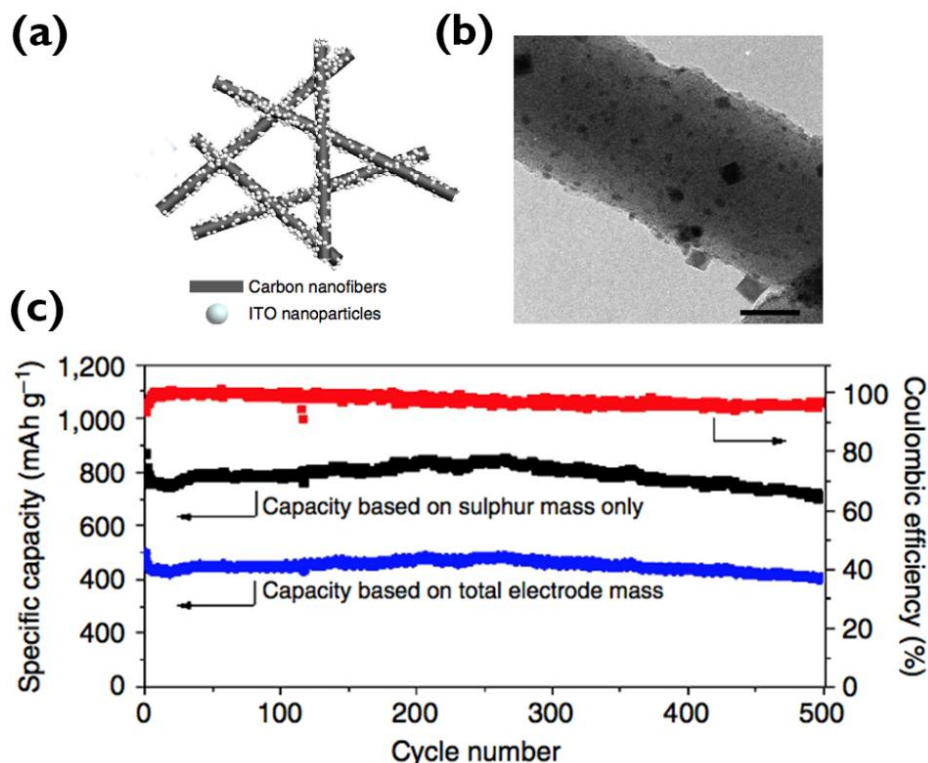


Figure 2.19: (a) Schematic and (b) TEM Image of ITO/CNF Composite; (c) Cycle-Performance of S/ ITO/CNF Composite^[142].

Recently, hybrid metal oxides/carbon has been considered another attractive matrix that provides both high conductive network and strong confinement of sulfur species. Zhang and coworkers used an in situ hydrolysis method to fabricate TiO₂ decorated hollow carbon nanofiber (HCNF)^[61]. The hybrid TiO₂/HCNF had a specific surface area of 62.5 m² g⁻¹ and a pore volume of 0.126 cm³ g⁻¹. Sulfur was homogeneously diffused into the TiO₂ layer by a thermal treatment. The as-prepared ternary S/TiO₂/HCNF composite with a sulfur loading of 67.5 wt % delivered an initial capacity of 1040 mAh g⁻¹ and had a capacity retention of 62.5 % after 200 cycles at a 0.5 C rate, which can be mainly attributed to the fast electron-transfer path provided by HCNF and efficient confinement of polysulfides enabled by porous TiO₂. Moreover, Cui and coworkers demonstrated a spatial control of sulfur species deposition on tin-doped indium oxide (ITO) decorated carbon nanofibers (CNFs) (Figure 2.19a and 2.19b)^[142]. Because of its high conductivity and hydrophilic surface, ITO nanoparticles on the CNFs can not only facilitate the redox kinetics of sulfur but also control the deposition of polysulfides and the growth of Li_xS. As a result, the composite maintained a specific capacity of 710 mAh g⁻¹ with capacity decay of 0.036% per cycle over 500 cycles (Figure 2.19c).

2.4.1.3 Polymers

Polymers, especially conductive polymers such as poly (3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy), polythiophene (PTh) and polyaniline (PANi), have been explored for hosting or coating sulfur. Generally, the synthesis of polymers involves an in-situ chemical polymerization in aqueous solution, which is favorable for surface modification of sulfur with low-melting point. In addition, polymers with unique chain-like structure and functional groups can chemically bind with sulfur, which can not only confine polysulfides effectively, but also relieve the stress arising from the volume change of sulfur cathode.

Core-shell design of sulphur-polymer composite

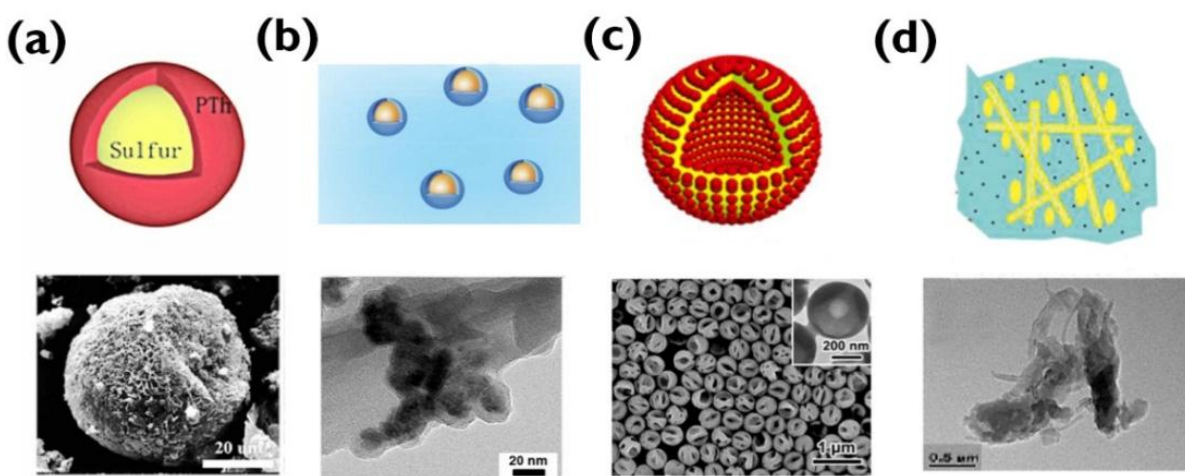


Figure 2.20: (a) S@PTh Composite^[143]; (b) Nano S@PEDOT Composite^[144]; (c) Hollow S@PVP Composite^[145]; (d) S@MWCNT-PNAi Composite^[146].

Polymer coating has been proved to be an effective approach to enhance the performance of sulfur cathode by forming a core-shell structure as shown in **Figure 2.20**. The functional polymer shell can not only facilitate the electron transfer to the electroactive sulfur core, but also protect it from physical and/or chemical changes. For example, Wu and coworkers coated a layer of porous conductive PTh on sulfur core through an in-situ chemical polymerization method (**Figure. 2.20a**)^[143]. The PTh shell acted as a conductive additive and a porous adsorbing agent, improving the sulfur utilization and polysulfides confinement. The core-shell structured PTh/S composite cathode had a good cycle life with a reversible capacity of 830.2 mAh g⁻¹ after 80 cycles.

To further enhance the sulfur utilization and rate capability, it is necessary to reduce the particle size of sulfur core. For example, ultrafine sulfur nanoparticles with a diameter in the range of 10-20 nm were prepared via a membrane-assisted precipitation technique, followed by PEDOT

coating (**Figure 2.20b**)^[144]. Nano sulfur core afforded a short electron and ion transfer path. Meanwhile, PEDOT shell played dual roles in preventing the agglomeration of sulfur during charging and the dissolution of polysulfides during discharging. Because of these merits, the S/PEDOT core/shell nanoparticles had an initial discharge capacity of 1117 mAh g⁻¹ and a stable capacity of 930 mAh g⁻¹ after 50 cycles. Recently, a hollow sulfur core was prepared by a chemical precipitation method using poly(vinylpyrrolidone) (PVP) vesiculate micelle as surfactant (**Figure. 2.20c**)^[145]. Although the rigid PVP shell was not conductive, it can mechanically enforce the sulfur core to expand inward into the hollow and enhance the stability of cathode during cycling. After 100 cycles, a reversible capacity of 931 mAh g⁻¹ was achieved with a capacity retention of 91%. Moreover, with a PEDOT coating layer, the S@PVP composite cathode showed a high reversible capacity of 849 and 610 mAh g⁻¹ at a current rate of 2 and 4C.

In addition, polymer coated S-carbon composites with core-shell structure also exhibited much improved cycle stability and rare capability over their bare counterparts. The coating of PANi on S/MWCNT composites remarkable enhanced the redox kinetics of sulfur, which was about twice that of S/MWCNT composite (**Figure. 2.20d**)^[146]. The porous PANi shell can absorb electrolytes in the bulk and keep them on the surface of cathode, reducing the diffusion distance of lithium ion. Recently, the attachment of PPy onto the surface of mesoporous carbon/sulfur has been proved to be able to inhibit the migration of polysulfides and offer lithium ion conductive channels. A reversible capacity of 860 mAh g⁻¹ was achieved after 100 cycles at 0.2C^[147].

Having the advantages of core-shell structure, polymer based yolk-shell architecture with large internal void has been designed to address the volumetric expansion of sulfur as well as polysulfide dissolution. Zhou and coworkers constructed a PANi-S yolk shell composite by vulcanization of its core-shell precursor at high temperature (**Figure 2.21**)^[148]. During vulcanization, a fraction of sulfur core was reacted with PANi shell to form cross-linked sulfide or disulfide bonds while internal void inside the shell was generated. Owing to the strong chemical confinement of sulfur and buffer for volume change, the yolk-shell structured PANi-S composite with a sulfur loading of 58 wt% maintained a stable capacity of 765 mAh g⁻¹ at 0.2 C after 200 cycles.

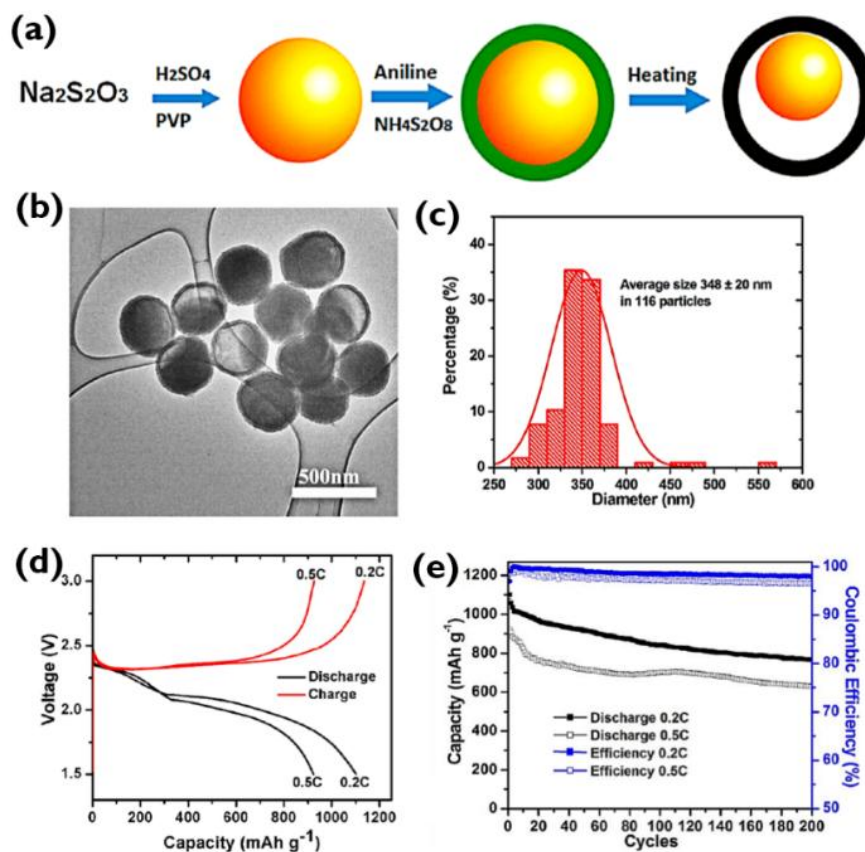


Figure 2.21: (a) Schematic of the Formation Process; (b) TEM Images; (c) The Particle Size Distributions; (d,e) Electrochemical Performance of Yolk-Shell S@PANi Composite ^[148].

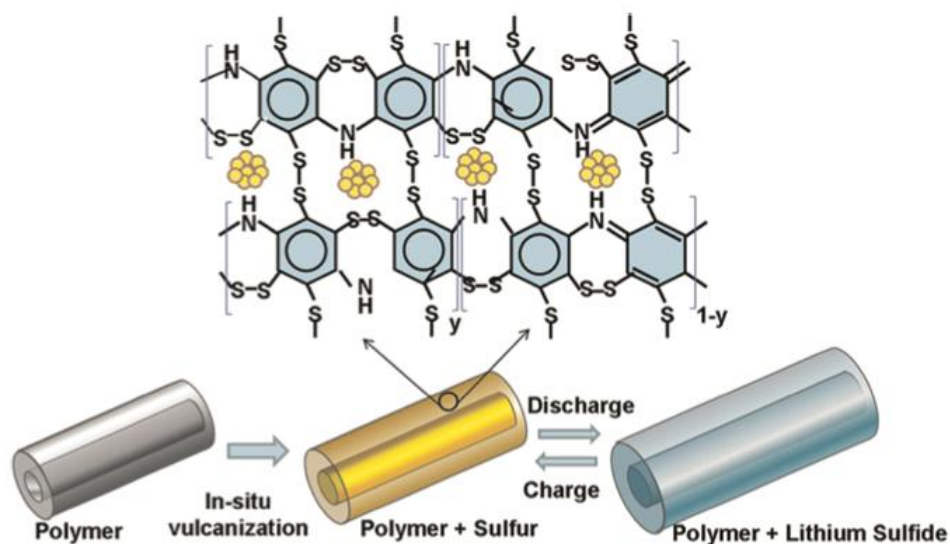


Figure 2.22: Illustration of the Construction and Discharge/ Charge Process of the SPANi-NT/S Composite.

Electro-active polymers can also be directly used as sulfur hosts due to their conductive chain-like backbone, tunable morphology and porosity. Self-assembled PANi nanotubes with a diameter of ~ 150 nm and a length of several micrometers were synthesized to host sulfur physically and chemically at molecular level^[55]. By a simple heat treatment, parts of sulfur can be embedded in the PANi backbone with inter-and/or intra-chain disulphide bonds through an in-situ vulcanization while others can either diffuse on the surface or infiltrate into the pores of the core-linked SPANi networks (**Figure. 2.22**). The dual confinement of sulfur and polysulfides by PANI matrix led to a stabilized capacity of 837 mAh g^{-1} after 100 cycles at a 0.1 C rate.

In addition, tubular-like PPy (T-PPy) fiber was developed by a self-degraded template method^[149]. Sulfur was homogeneously encapsulated into the hollow and pores of T-PPy, which provided conductive network for electron transport. The S/T-PPy composite with a sulfur loading of 30 wt % maintained a capacity of 650 mAh g^{-1} over 80 cycles. Branched S/PPy composite was also reported with enhanced sulfur utilization^[150]. However, both composites suffered from capacity decay because the low specific surface area of PPy matrix hardly suppressed polysulfides diffusion during cycling. One way to address this problem is to adjust the morphology of PPy together with surface modification. Recently, Liang and coworkers prepared a split-half-tubular PPy (SHT-PPy) using a chemical polymerization method, which had a much higher specific surface area than T-PPy^[54]. Sulfur was loaded on the surface of SHT-PPy by a chemical precipitation method. To prevent the direct contact between S and electrolytes, a layer of PPy was further coated on the SHT-PPy@S composite to form a three-layered structure. The internal SHT-PPy acted as conductive backbones to facilitate the reaction kinetic of sulfur while the external PPy coating served as physical barriers to mitigate polysulfides migration. As a result, the sandwiched SHT-PPy@S@PPy composite cathode exhibited a reversible capacity of 554 mAh g^{-1} after 50 cycles.

2.4.2 Interlayers

Modifying the configuration of Li-S batteries is another valid approach to enhance the performance. Since a decent sulfur host still can not fully stop the free polysulfides migration through separator, interlayers have been inserted between the cathode and separator to assist the trap of polysulfides. The use of interlayers as polysulfides inhibitor is presented below.

2.4.2.1 Carbon

Carbon based interlayers were well studied because of their lightweight and tunable pore structure. Similar to the function of carbon matrix in cathode, carbon interlayers play a key role in adsorbing polysulfides thanks to their porous structure. In addition, they act as an upper current collector and provide additional electron path for polysulfides reutilization. For example, a microporous carbon interlayer was prepared by simply mixing high-surface-area carbon black with polymer binder, followed by assembling with a sulfur cathode as shown in **Figure 2.23**^[151]. It dramatically decreased the charge transfer resistant of the sulfur cathode, leading to enhancement of active material utilization. Besides, it was found that the micropore of the inserted carbon interlayer got filled after cycling and no insulating S/Li₂S agglomeration was observed on the surface, implying an effective localization of polysulfides within the pore structure. As a result, this bi-functional interlayer contributed to improvement in capacity and cycle stability.

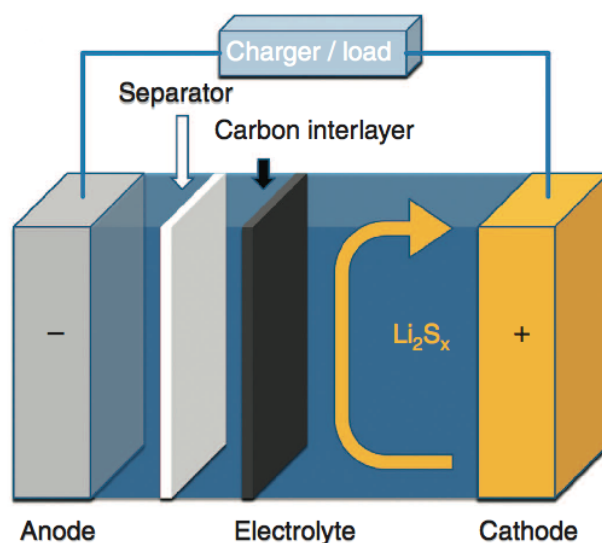


Figure 2.23: Scheme for the Li-S Batteries with a Bi-functional Microporous Carbon Interlayer^[151].

The texture of the carbon interlayers affects their ability in capturing polysulfides. For example, activated carbon nanofibers with tunable pore size were coated onto a polypropylene separator as polysulfide filters. The one with the greatest microporosity and the smallest pore size was the most effective for retaining polysulfides, which can be mainly attributed to the good absorbability of micropores^[152]. In addition, mesoporous carbon interlayer with tailored pore volume was papered by changing the amount of silica templates^[66]. The incorporation of mesoporous carbon interlayers with higher pore volume resulted in better capacity and cycle life of batteries, indicating that pore volume is one of the key factors in determining the extent of polysulfide absorption.

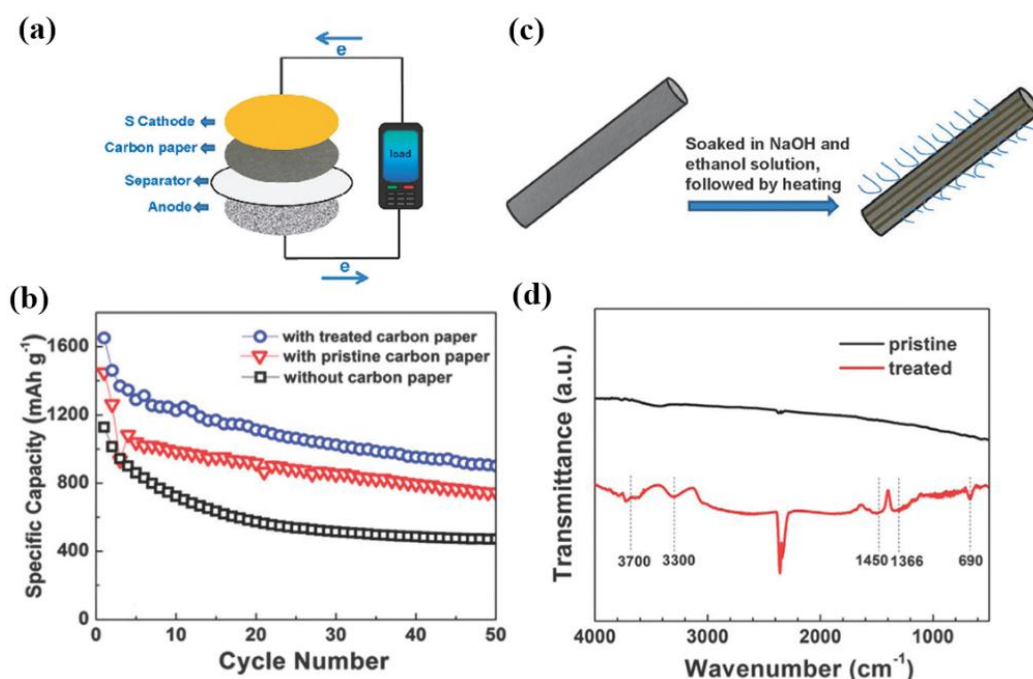


Figure 2.24: (a) Schematic of Li-S Batteries with a Carbon Paper Interlayer; (b) Comparison of Cycle Performance of Sulfur Cathode with Different Interlayers; (c) Scheme for the Surface Modification of Carbon Paper by NaOH Treatment; (d) FT-IR Spectrum of Carbon Paper before and after NaOH Treatment^[69].

Surface modification of carbon-based interlayers by functional groups or polymer coatings can further enhance the trapping of polysulfides. As shown in **Figure 2.24a** a free-standing carbon paper was inserted between a sulfur cathode and separator^[69]. Compared that the cathode with an untreated carbon paper and with no interlayer, the one with a sodium hydroxide (NaOH) treated carbon paper had much higher capacity and better cycle life (**Figure 2.24b**). The introduced hydroxyl functional groups and micro-cracks on the carbon paper by alkaline treatment (**Figure 2.24c and 2.24d**) improved the hydrophilicity and surface area of the carbon paper so that the highly polar polysulfides can be effectively trapped. Acid treatment is another way to functionalize carbon materials. A sulfonated acetylene black (AB-SO₃⁻) was coated on separator. The grafted

SO_3^- groups with negative charge can effectively reject polysulfide anions by electrostatic repulsion and mitigate the diffusion of polysulfides through separator^[153]. With the incorporation of the AB-SO_3^- coated separator, a sulfur cathode delivered a reversible capacity of 955 mAh g^{-1} after 100 cycles at 0.1C and had a capacity retention of 75.6%. Polymer coating can also adjust the surface properties of carbon and provide functional groups. For example, a poly(acylic acid)-coated single walled carbon nanotube (PAA-SWNT) interlayer was prepared^[154]. The carboxyl groups ($-\text{COOH}$) in the PAA chain can interact with polysulfides through hydrogen bond and suppress their diffusion. In addition, the casting of polyacrylonitrile (PAN) on carbon nanofiber interlayer enhanced the trapping of polysulfides due to interatomic attraction of the pyridine groups in PAN chains^[70].

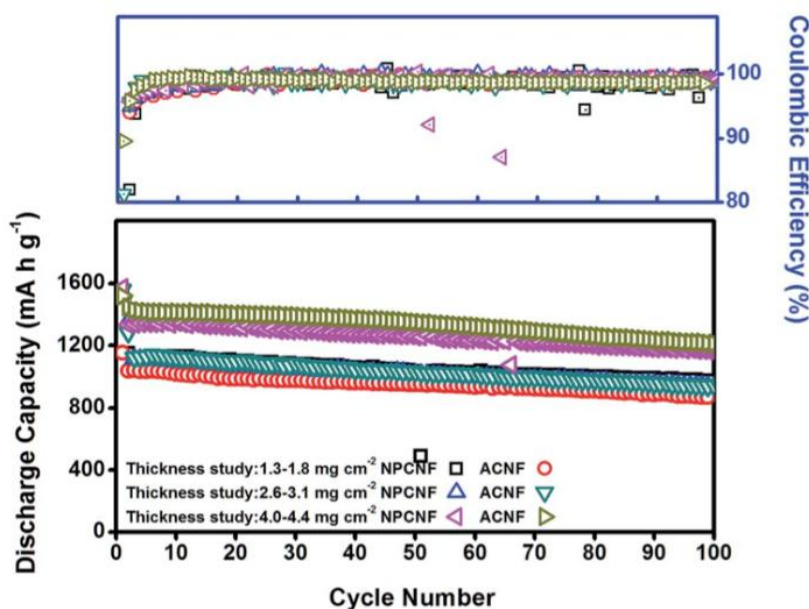


Figure 2.25: Comparison of Cycling Performance of Li-S Batteries with Varying Thicknesses of Activated CNF Interlayers.

The thickness of carbon based interlayers is another important factor that directly determines the effectiveness of polysulfides capture. Owing to the weak interaction between polar polysulfides and non-polar carbon interlayer, the migration of polysulfides is hardly suppressed with extended cyclings. Increasing the thickness of carbon interlayer is a facile method to tackle this problem by increasing the diffusion length for polysulfides. Improvement in cycle life was achieved as the thickness of a free-standing activated CNF interlayer was increased from 126 μm to 251 μm , corresponding to an increase in mass from 1.3-1.8 to 4-4.4 mg cm^{-2} (**Figure 2.25**)^[65].

2.4.2.2 Oxides

Metal oxides based interlayers are also very promising because the electronegative oxygen induced polar surface of metal oxides can absorb polysulfides through surface reaction/chemical interaction. Since the intrinsic brittle property of metal oxide makes it hard to get a free-standing membrane, various carbon supported metal oxide interlayers have been fabricated as alternatives. For example, a free-standing titanium oxide (TiO_2)/CNT paper interlayer has been prepared to suppress the diffusion of polysulfides by taking the synergistic effect of the physical barrier of CNT paper and the chemical effect of TiO_2 (**Figure 2.26**)^[155]. The flexible CNT paper is a mechanically strong substrate for TiO_2 growth and ensures good conductivity while the leaves-like structured TiO_2 can adsorb polysulfides via Ti-S and O-S binding, which mimics the adsorption of water molecules on the surface of leaves' cell. As a result, a sulfur/activated carbon composite cathode with this functional TiO_2 /CNT interlayer exhibited a stable cycle performance of 575.8 mAh g^{-1} and a high Coulombic efficiency of $\sim 99\%$ after 250 cycles. Recently, ultra-fine TiO_2 nano particles was decorated on a carbon nanofiber interlayer as anchors to capture polysulfides, which enabled a good cycle life with a capacity retention of 74.2% after 500 cycles for a common sulfur cathode ^[156].

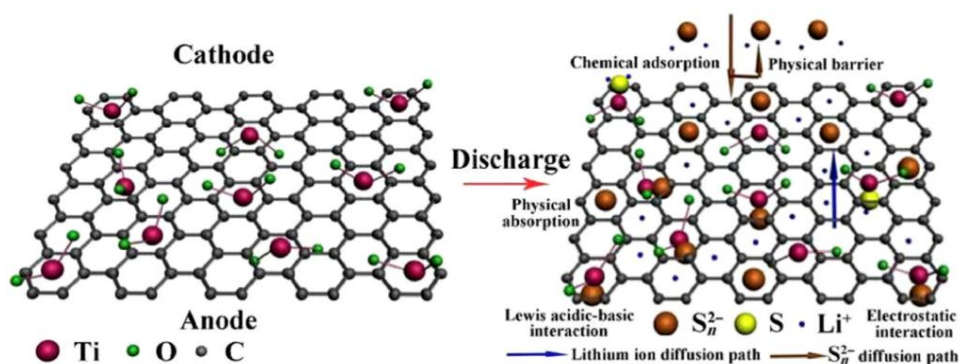


Figure 2.26: Illustration of the Function of TiO_2 /CNT paper Interlayer^[155].

Vanadium oxide (V_2O_5) is another attractive metal oxide that has a different polysulfides anchor mechanism from TiO_2 . A flexible interlayer consisting of V_2O_5 nanowires and CNT was prepared using a vacuum filtration method^[157]. Because of its high redox potential, V_2O_5 nanowires can oxidize polysulfides to thiosulfate and sulfate, which are bonded on its surface and serve as mediators to block polysulfides diffusion and regenerate them. CNT with a high aspect ratio can form self-assembled interconnected conductive pathways, which can reduce the charge-transfer resistance of the cathode and increase the sulfur utilization. Having a sulfur loading of 6 mg cm^{-2} ,

the cathode with the $\text{V}_2\text{O}_5/\text{CNT}$ interlayer exhibited an initial capacity of 1155 mAh g^{-1} and had a capacity fading rate of 0.34% per cycle over 100 cycles. In addition, flaky V_2O_5 was grown on electro-spun carbon fibers by a solvothermal method, followed by thermal treatment in air^[72]. The as-prepared $\text{V}_2\text{O}_5/\text{C}$ composite was used as a free-standing interlayer for a sulfur cathode with a sulfur loading of 2 mg cm^{-2} . A reversible capacity of 800 mAh g^{-1} with a capacity retention of 70.6% was achieved after 1000 cycles at a current rate of 3C , which is attributed to the chemical interaction between polysulfides and V_2O_5 as well as the fast electron and ion pathway provided by carbon nanofibers.

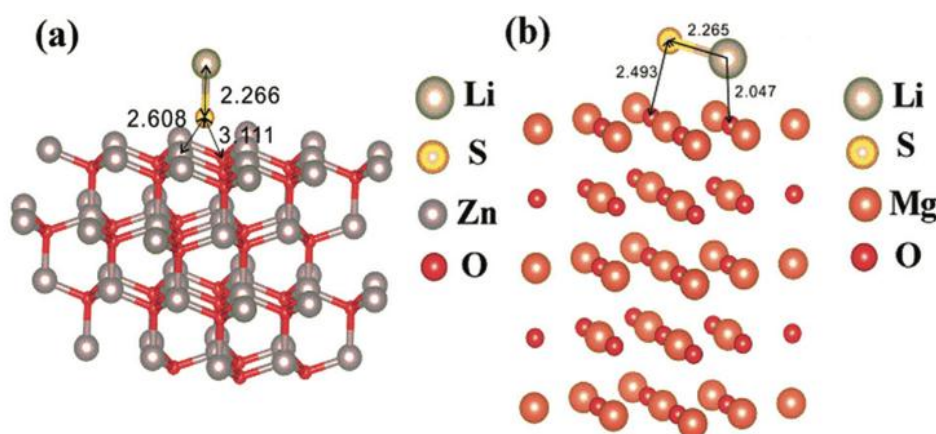


Figure 2.27: DFT Calculation of Binding Energies of $\text{Li-S}\cdot$ with (a) ZnO and (b) MgO ^[158].

Ultra-thin metal oxide film can also be directly coated on the surface of cathode using atomic layer deposition method. For example, a thin layer of zinc oxide (ZnO) or magnesium oxide (MgO) was coated on a reduced graphene oxide aerogel/sulfur composite cathode^[158]. It was found that both thin layers can constrain polysulfides within the cathode region, but ZnO exhibited a much stronger polysulfides affinity than MgO , having a binding energy of 5.4 eV (**Figure 2.27**). As a result, cathode with a ZnO layer showed better cycle stability with a capacity retention of 89% over 100 cycles. In addition, TiO_2 layer was also deposited on the surface of a nitrogen-doped graphene/S composite cathode using the same method for polysulfides diffusion control and negligible weight was added to the cathode systems^[60].

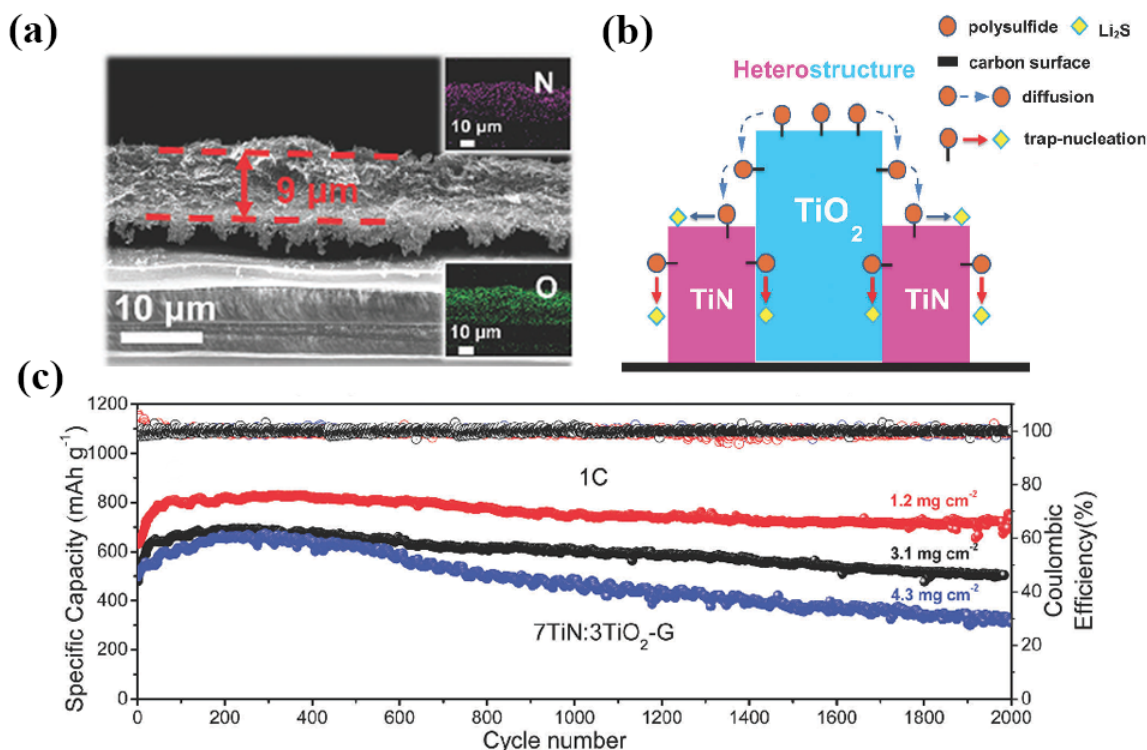


Figure 2.28: (a) Cross-Section SEM Image of TiO₂/TiN-Graphene Interlayer; (b) Scheme for the Twin-Born TiO₂/TiN Heterostructures on Graphene; (c) Cycle Performance of Batteries with TiO₂/TiN-Graphene Interlayer^[73].

Although metal oxides are capable of trapping polysulfides species via strong chemical binding, their poor conductivity is not favorable for effective reutilization of polysulfides. It was found that sulfur cathodes with a metal oxides/super P coating layer had lower capacity and faster capacity decay than that with a pure super P coating^[159]. The limited conducting area of the metal oxide/super P coating layer led to the formation of an additional dense film at the interface of the cathode and separator, which increased the internal charge-transfer resistance and deteriorated the performance. To solve this critical problem arising from the intrinsic properties of metal oxides, it is necessary to integrate nanostructured metal oxides with conductive frameworks to ensure fast electron transfer. Very recently, a twin-born TiO₂/titanium nitride (TiN) heterostructures were loaded on graphene to form an interlayer with a thickness of 9 μm (**Figure 2.28a**)^[73]. TiN is a polar conductor and has weaker binding affinity to polysulfides compared to TiO₂. Because of the interfacial contact between TiO₂ and TiN in the heterostructures, polysulfides trapped by TiO₂ can quickly diffuse to the conductive surface of TiN, where they are converted to Li₂S (**Figure 2.28b**). In addition, graphene can provide long-range conductive framework for the conversion reaction. By simply coating this interlayer on separator, a graphene-sulfur cathode with a sulfur loading of 3.1 mg cm⁻² maintained a reversible capacity of 503 mAh g⁻¹ after 2000 cycles at a 1C, corresponding to a capacity retention of 73% (**Figure 2.28c**).

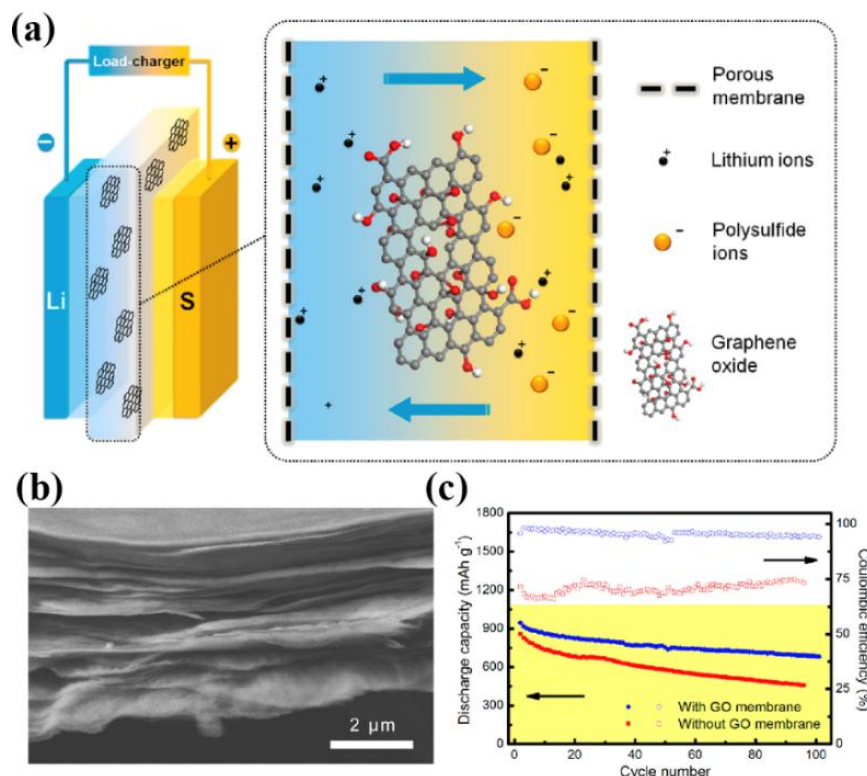


Figure 2.29: (a) Schematic of A Lithium-Sulfur Battery with the Incorporation of A GO Membrane; (b) Cross-Section SEM Image of GO Membrane; (c) Comparison of Cycle Performance of Batteries with and without GO Membrane^[160].

Considering their strong mechanical strength, excellent flexibility and ion selectivity, graphene oxide (GO) membranes are potential alternatives to metal oxide based interlayers. The negative surface charge of GO membrane can intrinsically repulse polysulfide anions by electrostatic interaction (**Figure 2.29a**)^[160]. By simply attaching a thin GO membrane (~5 μm, **Figure 2. 29b**) on a commercial polymer separator, the Coulombic efficiency of Li-S batteries was remarkably increased from 70 to 92% (**Figure 2.29c**), whereas the average value of lithium ion diffusion coefficient was slightly degraded, confirming that GO membrane are permselective to lithium ions against polysulfide anions. However, the poor conductivity of GO membrane inevitably hinders the utilization of active materials, resulting in low capacity. With the increase in thickness of GO membrane, obvious capacity decay was observed due to the higher charge transfer resistance and polarization. One facile way to address this problem is to control the thickness of GO membrane within a sub-micron range. By the inserting of a 0.75 μm thick, shear-aligned GO membrane, good active material utilization and capacity retention were achieved for a high-loaded sulfur cathode^[161]. Notably, the highly in-plane orientated GO membrane offers organized channels for fast ion flow and has negligible effect on rate performance. These results confirmed that GO membrane with controlled thickness and orientation is a promising polysulfides inhibitor.

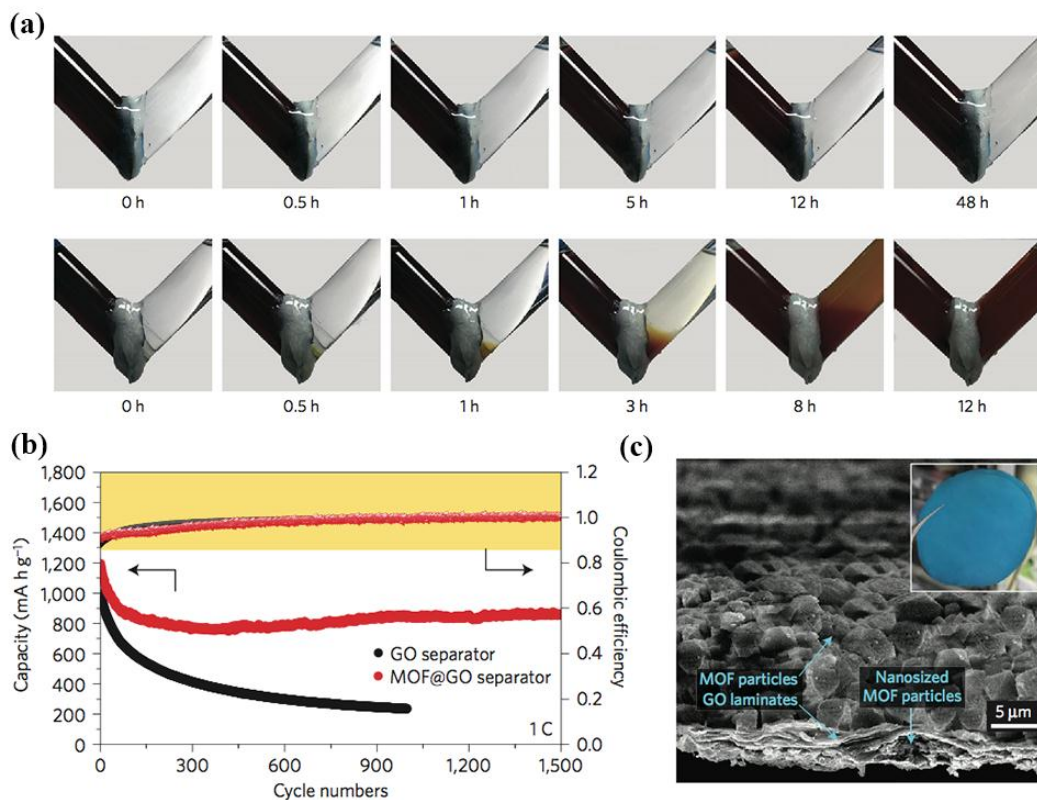


Figure 2.30: (a) Polysulfide Permeation Measurements for MOFs/GO (Upper) and GO (Lower) Membrane; (b) Comparison of Cycle Performance of Batteries with MOFs/GO and GO Membrane; (c) SEM Image of MOFs/GO Membrane^[162].

Recently, GO-containing membranes with hierarchical structure have attracted much attention. For example, metal organic frameworks (MOFs) with a pore window smaller than the length of long-chain polysulfides molecules was introduced into GO membranes as polysulfides sieves^[162]. Compared with GO membrane, the hybrid MOF/GO membrane was more effective in preventing the penetration of polysulfides solution on the basis of permeation experiments (**Figure 2.30a**). When evaluated as the separator for Li-S batteries, it enabled a capacity retention of approximately 71% over 1500 cycles for a carbon/sulfur composite cathode with a sulfur content of 70 wt%, which corresponded to a capacity decay rate of as low as 0.019% per cycle (**Figure 2.30b**). Such a stable cycle life can be mainly attributed to the pore frameworks and the structure stability of the MOF/GO membrane on separator. The in-situ growth of MOF filled the gap between GO laminates and prevent from detaching from the separator after deep cycles (**Figure 2.30c**).

A ternary layered separator consisting of Nafion, GO and polypropylene (PP) has been prepared in order to get high polysulfides selective separation and low internal transfer resistance^[163]. Each layer played different roles: (1) the external Nafion layer with abundant sulfonic acid groups acted as retarding layer and stops the crossover of polysulfides; (2) the sandwiched GO layer with ultra-

thin thickness (approximately 40 layers, $0.0032 \text{ mg cm}^{-2}$) served as physical barrier and covered the macro pore of routine PP layer; (3) the internal PP layer gives strong mechanical support.

Although the design of oxide based interlayers has advanced Li-S batteries toward practical application by retarding the diffusion of polysulfides in organic electrolyte, there is still a long way to go, in terms of effective utilization of confined active materials, synthetic procedure and cost.

2.4.2.3 Polymers

Polymers with suitable mechanical strength and conductivity are also potential alternatives as free-standing interlayers. For example, polypyrrole (PPy) is a well-known conductive polymer and has been widely used as a coating layer for sulfur cathodes. The nitrogen atom of PPy has lone electron pairs and can bind with lithium atom in polysulfides to form a separate π - σ coordination. Recently, PPy based interlayers have been employed as an outer polysulfides inhibitor. PPy film, which was prepared by self-assembly of individual PPy nanotube, was sandwiched with a common sulfur/Ketjen black (KB) composite as shown in **Figure 2.31**^[164]. The PPy nanotube layer enabled good adsorption of polysulfides and reduced the charge transfer resistance of the sulfur cathode. As a result, improvement in cycle life of batteries was achieved with a capacity of 712 mAh g^{-1} after 300 cycles at 0.5C. In addition, PPy was also integrated with a free-standing carbon paper with an optimized thickness of $300 \text{ }\mu\text{m}$ ^[71]. It was found that the incorporation of hydrophilic PPy on carbon paper facilitated the lithium ion diffusion and improved the rate performance.

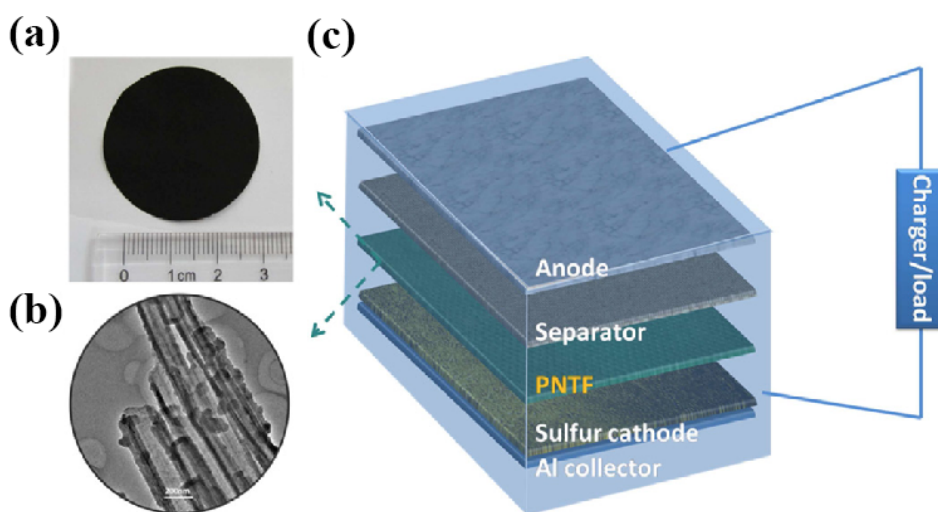


Figure 2.31: (a) Photograph and (b) TEM Images of the PPy Nanotubes; (c) A Schematic for the Rechargeable Li-S Batteries with the PPy Nanotube Interlayer^[164].

Another attractive polymer is bio-inspired polydopamine (PDA) that can easily deposit or coat on almost any substrate^[165]. It has many functional groups, including catechol, amine, and imine, most of which can act as polysulfides anchors. PDA modification of separators is a facile approach to mitigate the diffusion of polysulfides. For example, a hydrophilic separator was prepared by simple dip coating of PDA^[166]. The batteries with the PDA coated separator had a capacity approximately 30% higher than the batteries with a pure separator during the initial 30 cycles, which are attributed to the chemical interaction between the functional groups of PDA and polysulfides. In addition, the hydrophilic property of PDA-coated separator also enhanced the electrolyte uptake. Very recently, ultra-long cycle life of Li-S batteries has been achieved by a systematic effect from the coating of PDA on both the cathode and separator^[167]. A multi-lines of defense has been set to maintain the structure stability of cathode, trap of polysulfides within the cathode region as well as ensure fast Li^+ ion diffusion through separator.

2.5 The Specific and Volumetric Energy of Li-S Batteries at Laboratory Scale

The configuration of the lab-scaled Li-S cell is shown in **Figure 2.32**. The assembled cell generally consists of a 15 μm thick aluminum (Al) current collector, a 9 μm thick copper (Cu) current collector, a 25 μm thick polymer separator, a 100 μm thick S/C composite cathode and 100 μm Li anode. The average diameter of the electrodes and current collectors is around 1.1 cm while the diameter of separator is around 1.4 cm. Based on this configuration, the total volume and weight of the cell are approximately 2×10^{-5} L and 20 mg, respectively (Density value used: Al = 2.7 g cm^{-3} , Cu = 8.9 g cm^{-3} , Li = 0.53 g cm^{-3} ; Sulfur loading = 3 mg cm^{-2}). These results indicate the density of the assembled cell is around 1 kg L^{-1} . Given the complete utilization of S (1672 mAh g^{-1}) and an average working voltage of 2.1 V, the maximum practical specific energy and volumetric energy of the assembled cell is around 530 Wh kg^{-1} and 530 Wh L^{-1} , which is around 21.2 % and 18.9 % of their corresponding theoretical value.

Although the incorporation of functional interlayers with the cathode electrode can increase the capacity and cycle life of cells, it would reduce the specific energy and volumetric energy to some extent due to the additional weight and volume. For example, the maximum practical specific energy of the cell is reduced from 530 to 500 Wh kg^{-1} by simply introducing a carbon interlayer with an area density of 1 mg cm^{-2} . There is a trade-off between sulfur loading, interlayer mass and specific energy.



Figure 2.32 The Configuration of Li-S Batteries at Laboratory Scale

In this literature review, major advances in Li-S batteries have been summarized, including an overview of electrochemistry, technical challenges, development of nanostructured cathodes and interlayers and the practical specific and volumetric energy of Li-S batteries at laboratory scales. Insight into the multi-step redox mechanism of Li-S batteries has been given by using in-situ characterization techniques, which pave the way to find solution to the performance-related problems associated with sulfur chemistry. Various sulfur cathodes have been developed by using carbon, metal oxide or polymer as sulfur hosts in order to improve the conductivity of the cathode, trap polysulfides and accommodate the volume change of sulfur during batteries charging and discharging. Recently, new cell configurations has made a further leap in Li-S batteries due to the synergistic effect of nanostructured hosts and interlayers. Despite remarkable improvement in cycle performance and capacity, commercially-available Li-S batteries are still some years away. Much effort is needed to optimize the structural design and composition of interlayers for effectively absorbing active materials and keeping them reusable.

Chapter 3 Characterization Techniques

3.1 X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a common technique primarily used to determine the crystal structure of materials^[168]. X-rays are generated in a cathode ray tube by bombarding a target with high energy electron. Before directing to the sample, they are filtered to a monochromatic beam with a wavelength of λ , which is the characteristic of the target. When the incident X-rays pass through the sample, they will be scattered by the crystal lattice and form interference diffraction pattern at certain angles. The relation of interplanar spacing (d) to peak position (θ) is described by Bragg's Law (**Figure 3.1**):

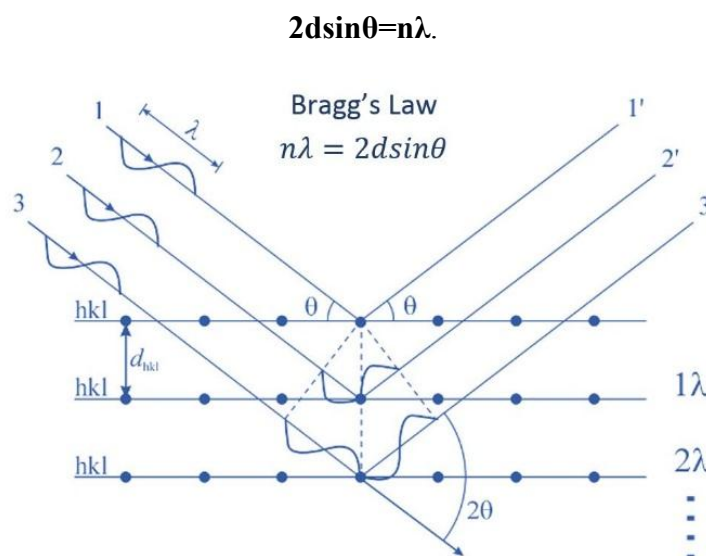


Figure 3.1: Bragg Diffraction Scheme.

If the condition is satisfied, constructive interference will occur. To obtain all possible diffraction directions of the lattice, the sample is rotated and scanned through a range of angles. Phase identification is the most important use of XRD because each crystalline material has its own unique diffraction pattern. Conversion of the peak positions to d -spacings gives information on unit cell dimensions. If a mixture has multi phases, each produces its characteristic pattern independent of the other.

In addition to phase identification, the particle size of nano-scale materials can be calculated using Scherrer equation.

$$\tau = K\lambda \beta \cos\theta$$

where τ is the grain size, K is the dimensionless shape factor and has a typical value of 0.9, β is the line broadening at half of maximum intensity, and θ is the Bragg angle.

3.2 Raman Microscopy

Raman spectroscopy is a vibrational spectroscopy technique that relies on the inelastic scattering of monochromatic light^[169]. It is used to observe vibrational, rotational, and other low-frequency modes in a system. Particularly, it is a popular and non-destructive tool for structural characterization of carbon materials because it is highly sensitive to even slight changes in orientation of symmetric C-C bonds. Every band in the Raman spectrum corresponds directly to a specific vibrational frequency of a bond within the molecule. For carbon materials, the D band is due to an A_{1g} breathing vibration of sp³-bonded carbon while G band is related to the coplanar stretching vibration of sp²-bonded carbon atoms. In addition, the relative intensity of the D band (I_D) and G band (I_G) in Raman spectrum provides the degree of graphitization and the size of any graphitic clusters present in disordered carbon.

3.3 Thermogravimetric Analysis

Thermal gravimetric analysis (TGA) is a thermal analysis technique that precisely measures the mass change of sample against temperature in a controlled atmosphere^[170]. It is used to investigate the thermal stability, phase change, degradation mechanism and chemical reaction during the heat treatment. A TGA consists of a sample pan, a programmable furnace, gas control and a precision balance. As it works, temperature is generally increased at a constant rate and an inert atmosphere might be selected in order to prevent the oxidation of sample or undesired reactions. As the temperature increases, the various components of sample decompose and the percentage of each can be calculated.

3.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is an imaging technique for surface morphology and chemical composition characterization^[171]. Electrons are generated from a gun by thermionic emission or field emission and are accelerated to an energy ranging from 5 to 20KeV. The electron beam then travel in a high vacuum environment and is focused on the specimen by adjusting electromagnetic lenses and apertures. The spot size of the beam is around 1-100 nm and is related to image

resolution. The interaction between electron beam and specimen mainly generate three kinds of signals, including backscattered electrons (BSE), secondary electrons (SE) and X-rays as shown in **Figure 3.2**.

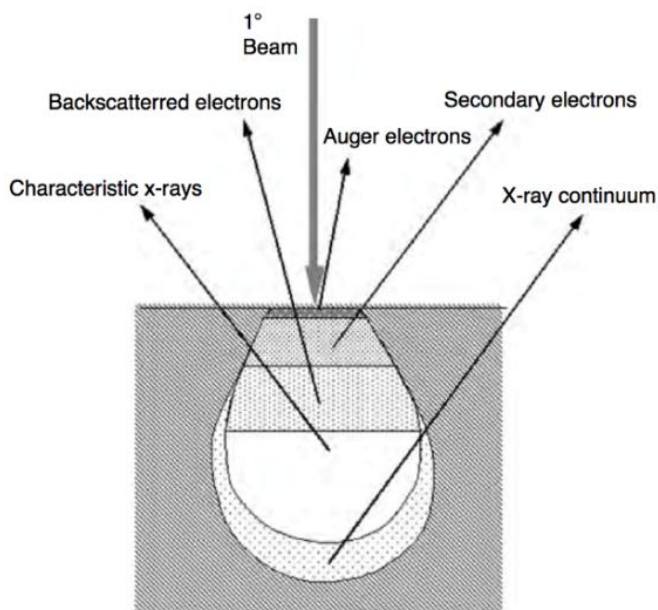


Figure 3.2: Schematic of Beam and Specimen Interaction and Signals Emitted From Different Parts of the Interaction Volume.

SE signals are generated by the incident beam knocking weakly bound valence electrons of the specimen out of their shell. They are used for the visualization of surface texture and roughness. BSE signals are incident electrons that are elastically scattered to a high angles ($>90^\circ$) via the interaction with the atomic nucleus of specimen and carry both compositional and topographic information. When incident electrons pass the specimen, inner shell electron of specimen is displaced by collision and X-rays are given off due to the migration of outer electron to an inner shell in order to return excited atom to ground state. The characteristic X-rays can be used to analyze the chemical information.

3.5 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is also an imaging technique that uses high energy electrons to pass through a thin specimen for investigating its crystal structure, orientation and chemical composition^[171]. TEM offers high spatial resolution in imaging down to individual atoms due to the small de Broglie wavelength of high speed electrons, which are usually accelerated to an energy of 200k eV, corresponding to a wavelength of 2.51 pm.

Electron lenses and apertures are used to magnify image and diffraction on the screen. There are two imaging systems in TEM: Imaging mode and diffraction mode. In imaging mode, objective aperture is used for bright field and dark field imaging. Bright field image is formed by selecting direct beam with objective aperture, whereas dark field image is formed when diffracted beam is selected. Dark field imaging is useful in studying crystal defect and crystallographic phases. In diffraction mode, selected area diffraction (SAD) aperture is used for obtaining a diffraction pattern. TEM image contrast can provide useful information on the thickness and composition of materials. Mass-thickness contrast and diffraction contrast are two important contrasts in bright and dark field imaging. Contrast arises from the selectively scattering of electrons through the imaging systems. Given a uniform thickness, the parts of specimen consisting of heavy atoms appear darker than that containing light atoms because of the strong interaction of electrons with heavy atoms. If all the atoms are the same, thick areas appear darker because most electrons are scattered. For diffraction contrast, crystalline areas of specimen appear darker due to the strong scattering of electron by Bragg diffraction.

3.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy is a surface sensitive chemical analysis technique with an average signal depth of about 3 nm^[172]. It is widely used to quantitatively analyze the valence state of element and composition of the constituents in the surface region. When a sample is irradiated with monoenergetic soft x-rays, electrons from approximately the first 20 atomic layers of the sample can be ejected. The binding energy of these emitted atoms is incident energy of X ray minus their kinetic energy, which corresponding to a series of peaks in an XPS spectrum.

3.7 Gas Sorption and Textural Characterization

Gas adsorption analysis is used to determine the surface area and porosity of solid materials^[173]. It is carried out by exposing samples to probe inert gas molecules, such as argon (Ar), carbon oxide (CO₂) and nitrogen (N₂) gas. Among them, N₂ is generally employed as the adsorptive and the test is conducted at around 77K (the boiling point of N₂) by recording the volume uptake of N₂ as a function of relative pressure, which is the ratio of the equilibrium (P_o) and the saturation pressure (P). The specific surface area of sample is evaluated from the gas adsorption isotherm based on a model proposed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938 for the first time. The BET theory, which consists of the first initials of their family names, applies to a multi-layer adsorption process which involves the adsorption of the probe molecules at different energy

sites on the surface as the pressure increases. To obtain precise and accurate specific surface area, the samples for BET analysis require outgassing before the physisorption measurement to remove molecular contaminants adsorbed on the surface of materials, such as gases or vapours.

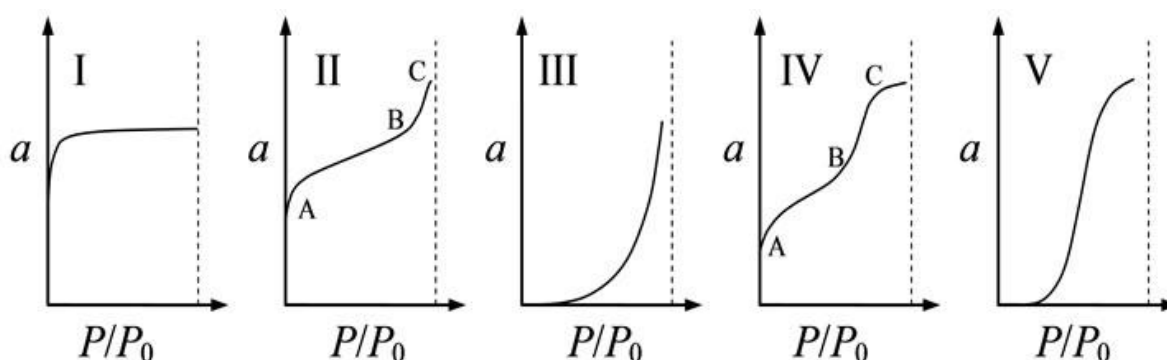


Figure 3.3: Five Different Types of Adsorption Isotherm.

There are five types of isothermal adsorption curves as shown in **Figure 3.3**. Type I isotherms result from the adsorption of gas molecules on microporous solid materials to form a single monolayer. Contrary to Type I, Type II isotherms are obtained due to the formation of indefinite multi-layer molecules on adsorbents which have a wide pore size distribution. Similar to Type II, Type III isotherms also show unlimited multi-layer formation process, but there is no indication when monolayer coverage is completed. Type IV and V isotherms have a characteristic hysteresis loop, which is caused by the capillary condensation occurring in mesopores. The difference between them is analogous to that between Types II and III.

Besides surface area, the pore size distribution and pore volume of materials can also be obtained by analyzing the adsorption and desorption branches of the isothermals via different methods. Barret-Joyner-Halenda (BJH) method is based on the assumption of cylindrical pore structure and is applied only to the mesopore and small macropore size range while density functional theory (DFT) calculation is used to get both microporosity and mesoporosity.

3.8 Electrochemical Measurements

Cyclic voltammetry (CV) is an electrochemical technique for studying the redox reaction of electrode^[174]. It is performed by sweeping the potential (**E**) of a working electrode at a certain scan rate and recording the current (**I**) as a function of potential (**I-E** curve). A working electrode is where redox reaction occurs and is usually coupled with a reference electrode of a constant makeup

and a fixed potential. The applied potential ramps linearly versus time and has a waveform, which can be repeated several cycles. The resulting current reflects electrode reaction rate and is governed by two main factors: (1) Mass transfer (2) Electron transfer at the electrode surface. In addition, surface adsorption or chemical reactions might also affect the kinetics of redox.

I-E curve contains lots of useful information about an electrode reaction, including the reversibility of redox, presence of intermediates and diffusion coefficient of analyte. Peak current and position are two important parameters. For a reversible, one-electron transfer redox, the ratio of cathodic current peak to anodic current peak is about 1 and the difference between the two peak potentials is about 59 mV.

Discharge-charge test is a common method to characterize the performance of batteries, including capacity, rate capability and cycle life. Generally, the test is conducted at a constant current rate (C-rate). 1C means the battery discharges its full capacity in one hour and 0.5C means it takes 2 hours. The discharge and charge curves (E-capacity) varies with C-rates. The higher a C rate is, the severer a polarization is, leading to a fast potential drop and a low capacity. Polarization is measured by overpotential (deviation from equilibrium value upon a faradaic current passing through the galvanic cell). There are two types of polarization: activation and concentration. Activation polarization is an overpotential caused by overcoming the energy barrier of rate-determining step of electrochemical reaction process. Concentration polarization occurs due to the formation of a mass diffusion layer near the electrode surface, which limits the reaction rate. C-rate also affects the number of charge-discharge cycles (cycle life) of batteries.

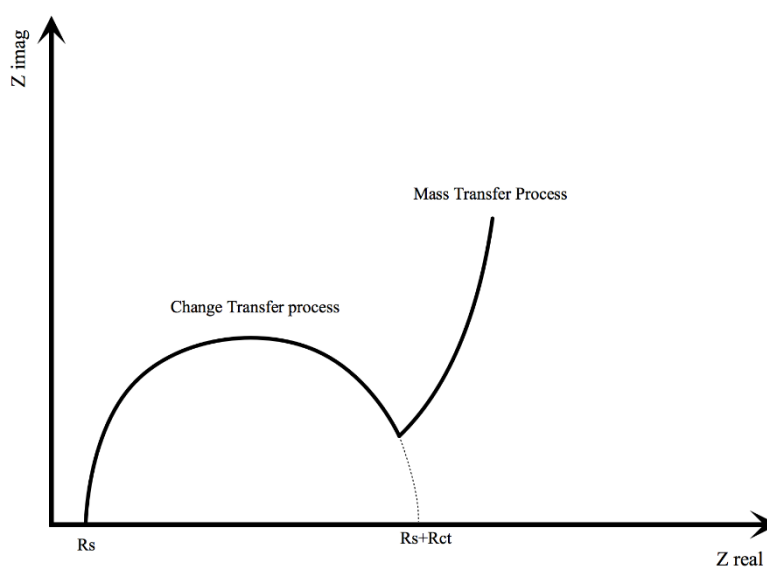


Figure 3.4: Schematic for a Common Nyquist Plot.

Electrochemical Impedance Spectroscopy (EIS) is a standard tool to investigate the internal resistance of batteries. It is measured by applying a sinusoidal potential to a steady-state cells and then recording the response current signals. The data can be presented in a Nyquist Plot where each point represents an impedance at a certain frequency. A common Nyquist plot consists of a semicircle at high frequencies and a short, inclined line in the low-frequency region, corresponding to the solution resistance, charge transfer resistance and Warburg impedance (**Figure 3.4**).

Specific capacity is calculated based on the active material mass using Faraday's law. For lithium-sulfur batteries with a theoretical capacity of 1672 mAh g^{-1} , 1C equates to a current of 1672 mA. Due to the low redox potential of lithium, the open-circuit voltage of lithium-batteries is around 3V. The cut-off voltage (the minimum allowable voltage) was set to 1.8V in order to ensure the cycle life of batteries. In this study, all cells were discharged and charged from 1.8–2.6 V at different C-rates using an electrochemical station (LAND, Wuhan) to test their cycle life.

Chapter 4 A Bio-inspired Polysulfides Adsorptive Interlayer Made from Zinc Oxide Nanowires for a Sulfur/Carbon Nanotube Cathode

4.1 Overview of the Work

Until now, limited research has been focused on employing metal oxide based interlayers to improve the performance of Li-S batteries because the intrinsic brittleness of metal oxide makes it very challenging to form a free-standing or flexible structure^[22]. Initially, porous nano-structured metal oxides were directly used as an additive in cathode, offering on-site adsorption of polysulfides, but these scattered absorption sites cannot ensure high active utilization due to the semi-conductive nature of metal oxides^[135]. To use metal oxides as an effective polysulfides adsorbent for the interlayer, it is, therefore, necessary to integrate them with a robust and interconnected conductive framework, which offers both mechanical support and fast electron transfer path for the utilization of the adsorbed polysulfides.

In this chapter, inspired by the brush-like membrane of cells for nutrient adsorption, a similar structure of interlayer consisting of zinc oxide nanowires and conductive frameworks has been designed for chemical adsorption of polysulfides in organic electrolytes. A proof of concept for polysulfides adsorptive brush has been initially demonstrated by sandwiching a sulfur/multi-walled carbon nanotube (MWCNT) composite cathode with a zinc oxide (ZnO) nanowires/nickel (Ni) foam interlayer, as this configuration is readily achieved with the appropriate pore morphology, adsorption ability, and structure stability. The chemical role of zinc oxide nanowires in anchoring polysulfides has been revealed by the analysis of the morphology and composition of cycled interlayer, as well as the theoretical density functional theory (DFT) calculation of binding energy of ZnO and five relevant S-based species. Based on the successful demonstration, a functional and much lighter and thinner interlayer has been made by integrating ZnO nanowires with a carbon (C) nanofiber mat for practical application of Li-S batteries.

The findings are reported in *Advanced Functional Materials* and featured on its back cover: **T. Zhao**, Y. Ye, X. Peng, G. Divitini, H.K. Kim, P. R Coxon, K. Xi, Y. Liu, C. Ducati, R. Chen, R. V. Kumar, *Adv. Funct. Mater.* **2016**, 26, 8418.

4.2 The Methods

4.2.1 Chemical Bath Deposition of ZnO Nanowire Arrays on Nickel Foam

Commercially-purchased nickel foams were pressed and cut into circular disks with an average diameter of 11 mm and thickness of 0.5 mm, followed by rinsing with deionized water and ethanol. Prior to the growth of nanowire arrays, a piece of treated Ni foam was initially wet with several droplets of 0.005M zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in ethanol and then annealed at 300 °C to form a seeding layer of ZnO nano crystals. This seeding treatment was repeated three times. The ZnO-seeded Ni foam was then put in a 20 ml aqueous solution of 0.05 M zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 0.025 M, hexamethylenetetramine (HMTA), 0.45 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 5mM polyethylenimine (PEI), followed by heating at 95 °C for 24h in an oven. Finally, the sample was collected and rinsed repeatedly with deionized water. Calculated by the mass change in the Ni foam before and after ZnO growth, the area density of ZnO nanowires was approximately 6 mg cm^{-2} .

4.2.2 Thermal Infusion of Sulfur on the Surface of MWCNT

The core-shell structured S/MWCNT composites were prepared using thermal infusion method. Briefly, 0.7g S was first mixed well with 0.3g MWCNT (Specific surface area 160-200 $\text{m}^2 \text{g}^{-1}$, diameter 10-30 nm, length >2 μm , purity>97%) and sealed in a polytetrafluoroethylene container under the protection of Ar gas, which was then transferred to furnace and heated at 150 °C for 24h.

4.2.3 Fabrication of Electron-spun PAN Derived Carbon Nanofiber

5g Polyacrylonitrile (PAN) with an average molecular weight of $M_w = 150,000 \text{ g/mol}$ was dissolved in 9 ml N,N-dimethylformamide (DMF) to form a 10 wt.% solution by constant stirring for 24h. Then, the readily polymer solution was loaded into a syringe with a stainless nozzle (0.6 mm diameter) for electrospinning process. The applied voltage was set at 20 kV, and the flow rate of solution was 1 mL h^{-1} . The as-electrospun nanofibers with a thickness of $\sim 50 \mu\text{m}$ were collected with an aluminum foil (10 cm×10 cm) located 20 cm away from the tip of the nozzle after 1h. The peeled PAN nanofiber was initially stabilized in air at 280 °C for 3h, followed by carbonization and activation at 1000 °C under a low oxygen-containing nitrogen atmosphere for 6 hours.

4.2.4 Growth of ZnO Nanowires on Carbon Nanofiber

Zinc oxide nanowires were grown on the as-prepared carbon nanofiber using the same chemical bath method, which were then cut into circular disks with an average diameter of 11 mm and mass of $\sim 1.3 \text{ mg cm}^{-2}$

4.2.5 Theoretical Calculation

Theoretical calculations were performed using Materials Studio 5.5 (Accelrys). The atomic configurations and binding energies were calculated using DFT within the Perdew–Berke–Ernzerh functional of generalized gradient approximation basis set. A $7 \times 7 \times 2$ supercell was employed to model ZnO and ZnO-Li₂S_n structures. Brillouin zone was sampled by a $2 \times 1 \times 1$ k-point Monkhorst-Pack grid. An energy cutoff of 400.0 eV was used to describe the interactions. All atoms were fully relaxed when the following convergence tolerance was met: the residual forces on the constituent atoms became smaller than $0.03 \text{ eV \AA}^{-1}$ and the maximum atomic displacement was higher than $0.005 \text{ \AA}$.

4.3 Microstructure and Morphology Characterization

4.3.1 Multi-walled Carbon Nanotube/Sulfur Composite Cathode

The Multi-walled carbon nanotube/sulfur composite (MWCNT/S) was rationally chosen to prove the role of interlayer in trapping polysulfides as it suffers from severe capacity decay due to the direct contact of sulfur to electrolyte. Previously, it was found that the cathode with a sulfur loading of 70%wt only had a capacity retention of 41.8% after 100 charging/discharging cycles^[128]. Although the one dimensional (1D) MWCNTs offers fast path for electron and ion transfer, their small specific area and pore volume can not accommodate sulfur species properly, leading to fast active materials loss in the electrolytes.

In fact, carbon nanotubes are a very attractive sulfur host, in terms of large-scale production^[175]. The incorporation of S with carbon nanotubes can be readily achieved by simply mixing and heating because of the low melting point of sulfur. In nature, elemental sulfur exists as the stack of crown-like S₈ with an orthorhombic crystal structure^[100]. Up on mild heating, it can slowly convert to monoclinic S₈ at round 95 °C and maintain solid. When the temperature reaches 115 °C, monoclinic S₈ starts melting and gradually becomes a mobile liquid, which has the lowest viscosity at the temperature of 150 °C. Because of this intrinsic property of sulfur, thermal infusion is a facile and valid approach to prepare sulfur-containing composites. In addition, carbon nanotubes are commercially available and their textures can be easily controlled, such as diameter, length, conductivity and mechanical strength.

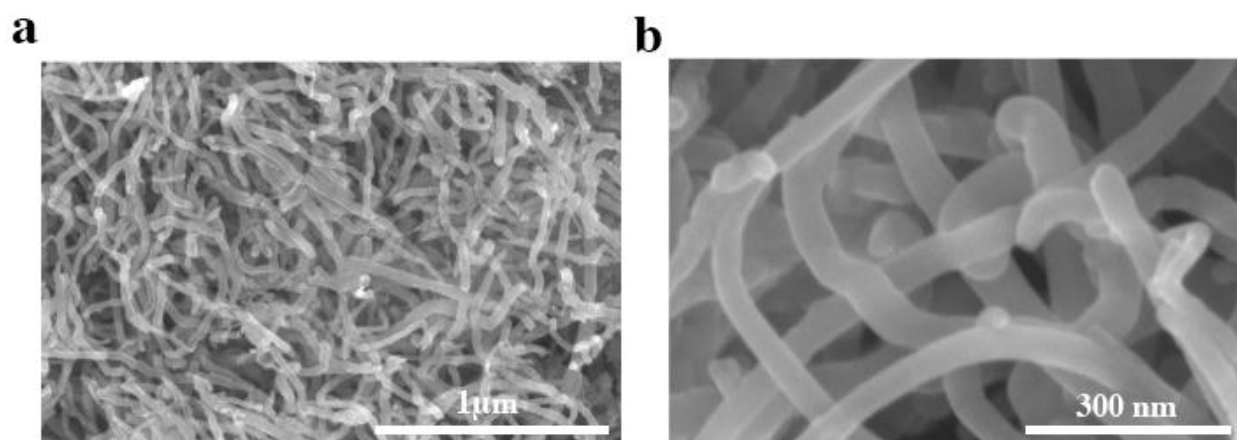


Figure 4.1: (a) Low and (b) High magnification SEM images of S/MWCNT Composite Cathode.

A MWCNT/S composite was prepared by thermal infusion method. To characterize its structure morphology, SEM was conducted on the samples. **Figure 4.1a and 4.1b** shows the low and high magnification SEM images of MWCNT/S composite. After the introduction of S, the surface of carbon appeared darker and a uniform core-shell structure was achieved. Generally, core-shell structured materials have multi-functionality. Here, MWCNT acts as the conductive backbone to offer electron transfer path from/to sulfur shell. The diameter of the MWCNT/S was about 60 nm and no sulfur agglomeration was observed, indicating the intimate contact between sulfur and carbon nanotubes due to their similar hydrophobic nature.

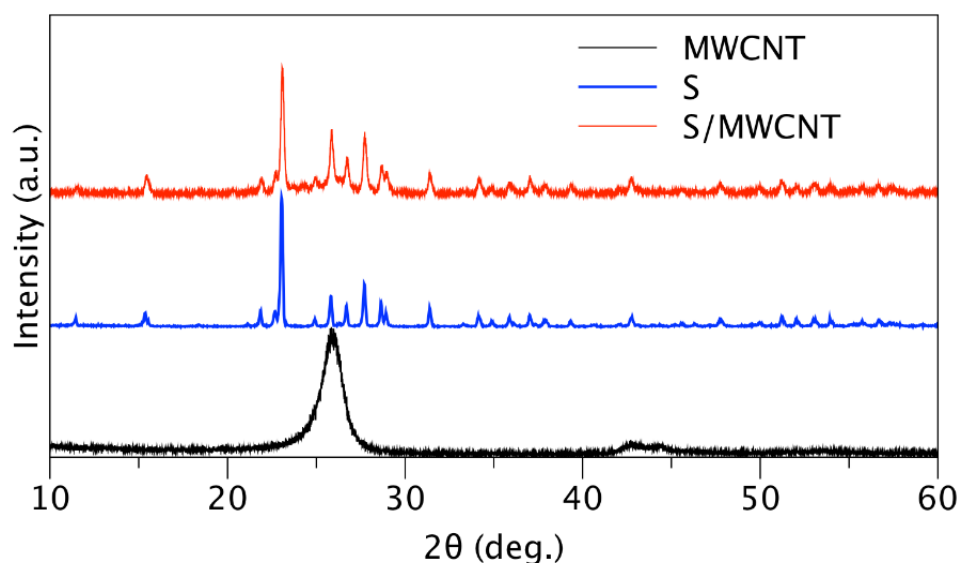


Figure 4.2: XRD Spectra of S/MWCNT Composite, S and MWCNT.

To reveal the crystal structure of the MWCNT/S composite, **Figure 4.2** shows XRD spectrum of MWCNT, S and MWCNT/S composite, respectively. MWCNT showed a slightly broad and prominent peak at around $2\theta = 26^\circ$, assigning to (002) plane while two overlapped peaks were observed around $2\theta = 42^\circ$, corresponding to (100) and (101) peaks. Elemental S had an Fddd orthorhombic structure with two characteristic peaks, at $2\theta = 23^\circ$ and 28° . The MWCNT/S composite exhibited a similar pattern to elemental S, indicating that sulfur coated well on carbon nanotube and no phase transformation happened during thermal infusion. The intensity of MWCNT peaks were weak in the spectra of the composite because of the high surface loading of sulfur.

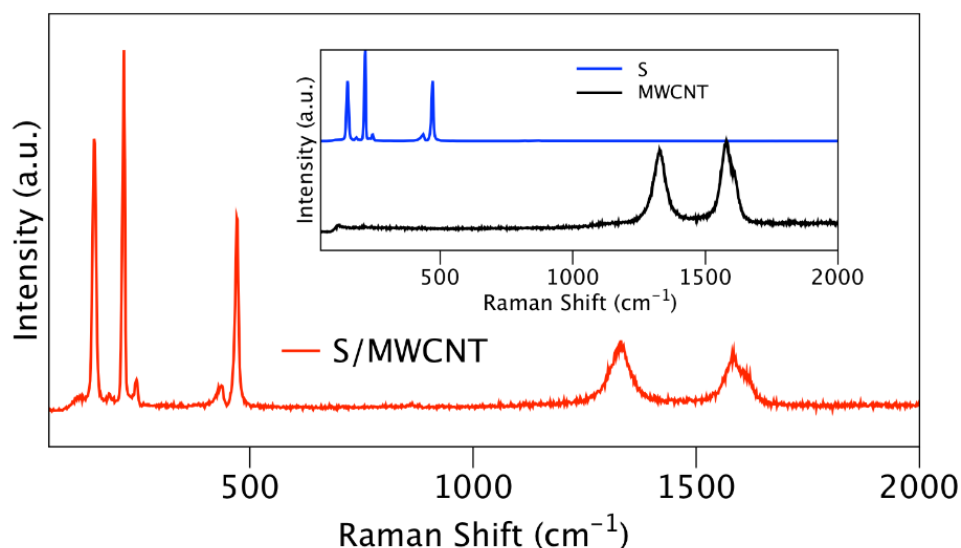


Figure 4.3: Raman Spectra of S/MWCNT Composite, S and MWCNT.

To further investigate the structural features of MWCNT/S composite, **Figure 4.3** shows the Raman spectrum of MWCNT, S and MWCNT/S composite, respectively. MWCNT exhibited two typical peaks, the G band and D band. The D band at around $\sim 1350 \text{ cm}^{-1}$ is assigned to defects and disorder in the MWCNT. The G band at $\sim 1580 \text{ cm}^{-1}$ is related to the coplanar vibration of sp^2 bonded carbon atoms in MWCNTs. The intensity of D band and G band were of similar magnitude, indicating the MWCNT is only partially graphitized due to multiple graphite layers. Elemental S had several characteristic peaks below 500 cm^{-1} , corresponding to the vibrations of S-S bonds^[176]. Except the aforementioned typical peaks from S and MWCNT, no other peaks were observed in the spectrum of MWCNT/S composite, indicating that S was just physically adsorbed on the surface of MWCNT.

The sulfur cathode slurry was prepared by mixing the as-prepared S/MWCNT composite, carbon black and polyvinylidene fluoride (PVDF) binder at a ratio of 7:2:1 in N-methyl-2-pyrrolidinone (NMP), which was then spread on aluminum foil via doctor blade. Carbon black was added to improve the electric connectivity between S/MWCNT composite while PVDF was used to ensure the adhesion of active materials to Al current collector, which serves as the mechanical support for the pasted active layer and remains electrochemically stable at working potentials. Except S/MWCNT composite, other components are considered as inactive mass in the batteries. Therefore, their ratio was optimized for high energy density of the batteries. The wet cathode was dried at 60°C for 24h to remove solvents and then cut into disc with a diameter of 11 mm. **Figure 4.4** shows the photograph (inset) and SEM images of the sulfur cathode. It can be seen that the cathode was quite uniform and pinhole-free, which is important for the stability of

cathode during batteries charging and discharging. The cross-section SEM image shows that the cathode was well compacted and had a thickness of about 100 μm . In addition, pores were evenly distributed throughout the cathode, facilitating the penetration of electrolyte and thus the mass transfer of lithium ions.

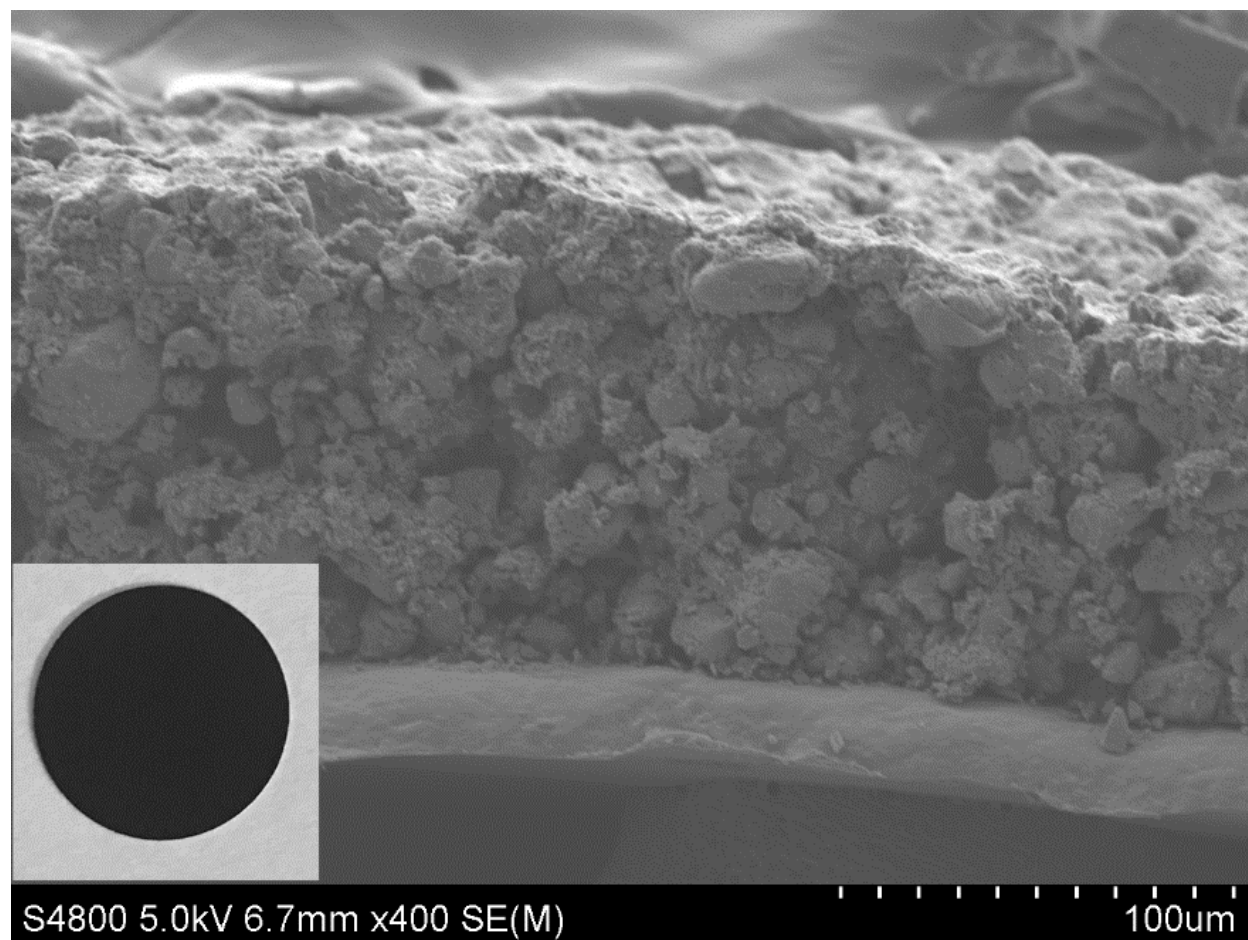


Figure 4.4: Photograph (Inset) and Cross-Section SEM Image of S/MWCNT Composite Cathode with a S Loading of $3\text{mg}/\text{cm}^2$.

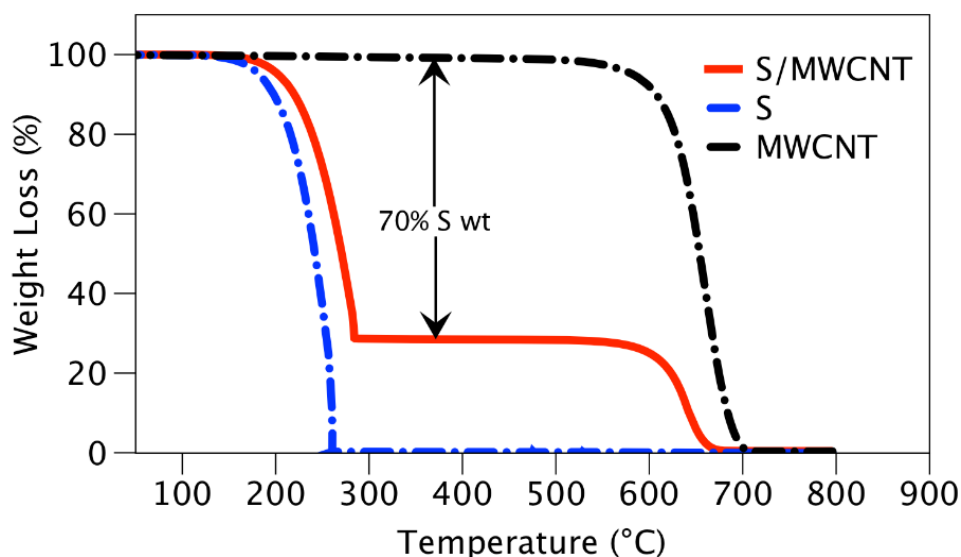


Figure 4.5: TGA Curves of S/MWCNT Composite, S and MWCNT.

Figure 4.5 shows the TGA curves measured for S, MWCNT and MWCNT/S composite. The curve of MWCNT/S exhibited two stages of mass loss. The one starting from 150 °C is due to the evaporation of S. Because of the physical adsorption of MWCNT, the evaporation of S anchored on the MWCNT surface was slightly slower than that of pure elemental S. Another mass loss stage ranging from 600 °C-700 °C is attributed to the combustion of MWCNTs. Based on the analysis of TGA results, the sulfur content of MWCNT/S was about 70 wt%. Generally, the areal S loading has to reach the range of 3-7 mg cm⁻² in order to meet the energy demand for practical applications. However, it is very challenging to make a uniform electrode without any cracking or pinholes due to the severe volume shrinkage of cathode slurry during drying. For a S/MWCNT composites cathode with a S content of 70 wt%, the areal S loading of 3 mg cm⁻² was about the maximum for a crack-free electrode.

4.3.2 Zinc Oxide/Nickel Foam Interlayer

Zinc oxide (ZnO) nanoparticles had been used as an additive in S-containing cathodes and interlayers to improve the cycle stability of Li-S batteries^[158, 177]. It is demonstrated that ZnO has a strong affinity to polysulfides by the chemical interaction between Li and O and can effectively trap them. However, ZnO is a semi-conductor and intrinsically can not ensure fast electron transfer. In addition, nanoparticles have many grain boundaries, which will inevitably increase the internal resistance.

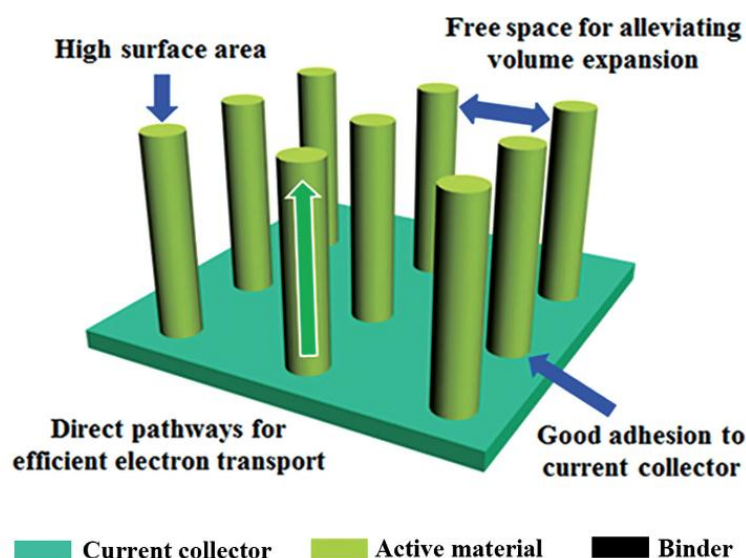
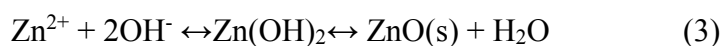
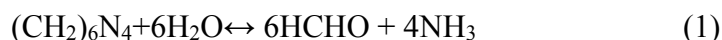


Figure 4.6: Illustration of the Advantages of 1D Nanowire Arrays on Current Collector^[178].

In this study, well-ordered nanowire arrays grown on two kinds of conductive substrates were prepared to overcome the aforementioned problems. As shown in **Figure 4.6**, the one-dimensional (1D) architecture of nanowires can offer continuous path for electron transport along their long axis^[178]. Besides, each nanowire is directly contacted with a conductive network, further increasing the efficiency of electron transfer. Last but not least, the space between neighboring nanowires allow for the diffusion of ions in electrolyte.

The growth mechanism of ZnO nanowire arrays on various substrates has been well studied^[179-181]. First, seeding of textured zinc oxide nano-crystals with their c axes normal to the substrate is an important step to control the orientation of the nanowires. Second, the thickness of the seeding layer determines the density of nanowire arrays, whose variation is accompanied by the change of the diameter and length of single zinc oxide nanowire. Third, the aspect ratio of zinc oxide nanowires can be tailored by adding surfactant to hinder the lateral growth of nanowires in solution.

Here, the growth of ZnO nanowires on the nickel (Ni) foam was achieved through chemical bath deposition. Commercially-available Ni foam is an ideal substrate to investigate the chemical effect of ZnO on soluble polysulfides, considering its limited physical adsorption abilities and robustness for postmortem analysis after cycling. Besides, it has good conductivity and acts as a 3D current collector. ZnO seeds were initially coated on the Ni foam by thermal decomposition of zinc acetate in air, which acquires a preferred orientation on the substrate in order to minimize surface energy^[181]. Then, the seeded Ni foam was immersed in an aqueous solution containing zinc nitrate, hexamethylenetetramine (HMTA), $\text{NH}_3 \cdot \text{H}_2\text{O}$ and polyethylenimine (PEI). The growth of ZnO nanowires is due to the hydrolysis of zinc nitrate accompanied by the following chemical reactions^[182]:



HMTA ($(\text{CH}_2)_6\text{N}_4$) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ provide OH^- to the solution, which can react with the Zn^{2+} precursor to induce the nucleation of ZnO and thus the growth of nanowires. PEI is a common surfactant that can adsorb onto the non-polar faces of ZnO and enhance the vertical growth (**Figure 4.7**).

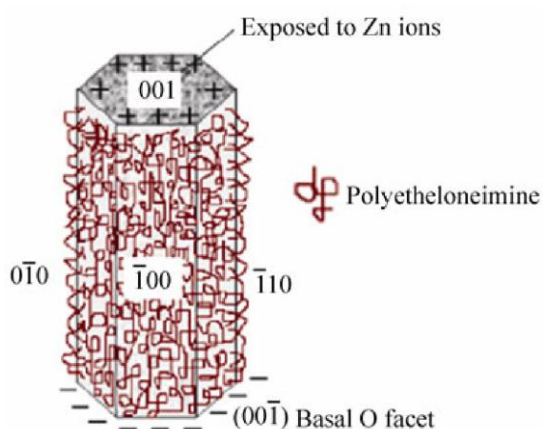


Figure 4.7: Illustration of the Effect of PEI during Synthesis of ZnO Nanowires^[182].

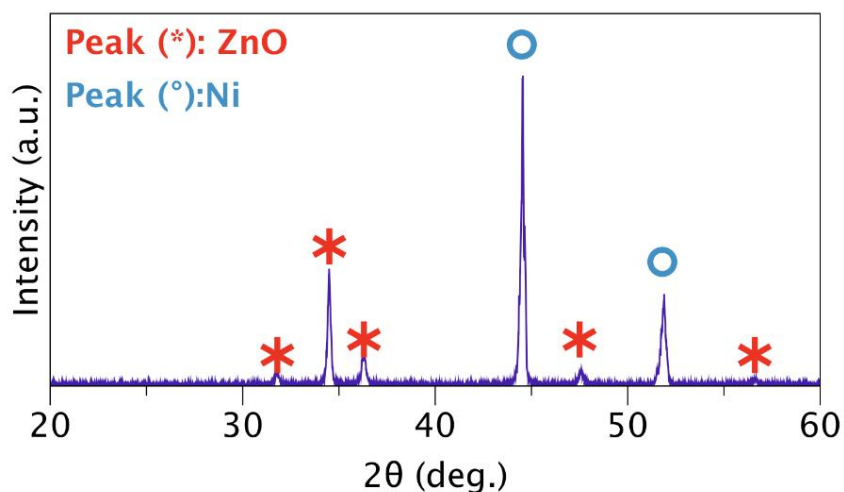


Figure 4.8: XRD Spectrum of ZnO Nanowire/Ni Foam Interlayer.

XRD was undertaken to investigate the crystal phase of the hybrid ZnO nanowires/Ni foam interlayer. As shown in **Figure 4.8**, except for the peaks assigned to Ni, the residual peaks were unambiguously indexed as the hexagonal wurtzite phase of ZnO with a lattice constant of $a=b=3.2498 \text{ \AA}$, $c=5.2066 \text{ \AA}$. The distinct peak at around $2\theta = 34.43^\circ$ is assigned to the (002) plane, implying the growth of ZnO nanowires along the c-axis perpendicular to the surface of Ni foam. In addition, this peak is quite sharp, reflecting that the prepared ZnO nanowires were highly crystalline.

After the integration of ZnO with Ni foam, the colour of Ni foam changed from bright to grey, (**Figure 4.9a inset**). **Figure 4.9 a-b** show the top-view and cross-section scanning electron microscopy (SEM) images of the ZnO nanowires/Ni foam interlayer. The 3D macroporous structure of Ni foam, with a thickness of $500 \mu\text{m}$, can be clearly seen from low magnification images (**Figure 4.9c**). Closer SEM observations at much higher magnification reveal the 1D nano architecture of ZnO, covering each strip of Ni foam with features having a diameter of 150 nm and a length of $2.5 \mu\text{m}$ (**Figure 4.9d-e**). Electron energy dispersive spectroscopy (EDS) (**Figure 4.9f**) further confirms the uniform distribution of ZnO nanowires on the 3D macroporous structure of the Ni foam. Based on the analysis of mass change of interlayer before and after ZnO growth, the areal loading of ZnO on the Ni foam was determined to be about 6 mg cm^{-2} . Thus, a unique structure is created by combining locally high surface area 1D ZnO nanowire arrays grown and anchored in a brush-like morphology on a large pore volume 3D Ni foam for optimizing chemical interaction with the soluble polysulfides from the electrolyte-solvent.

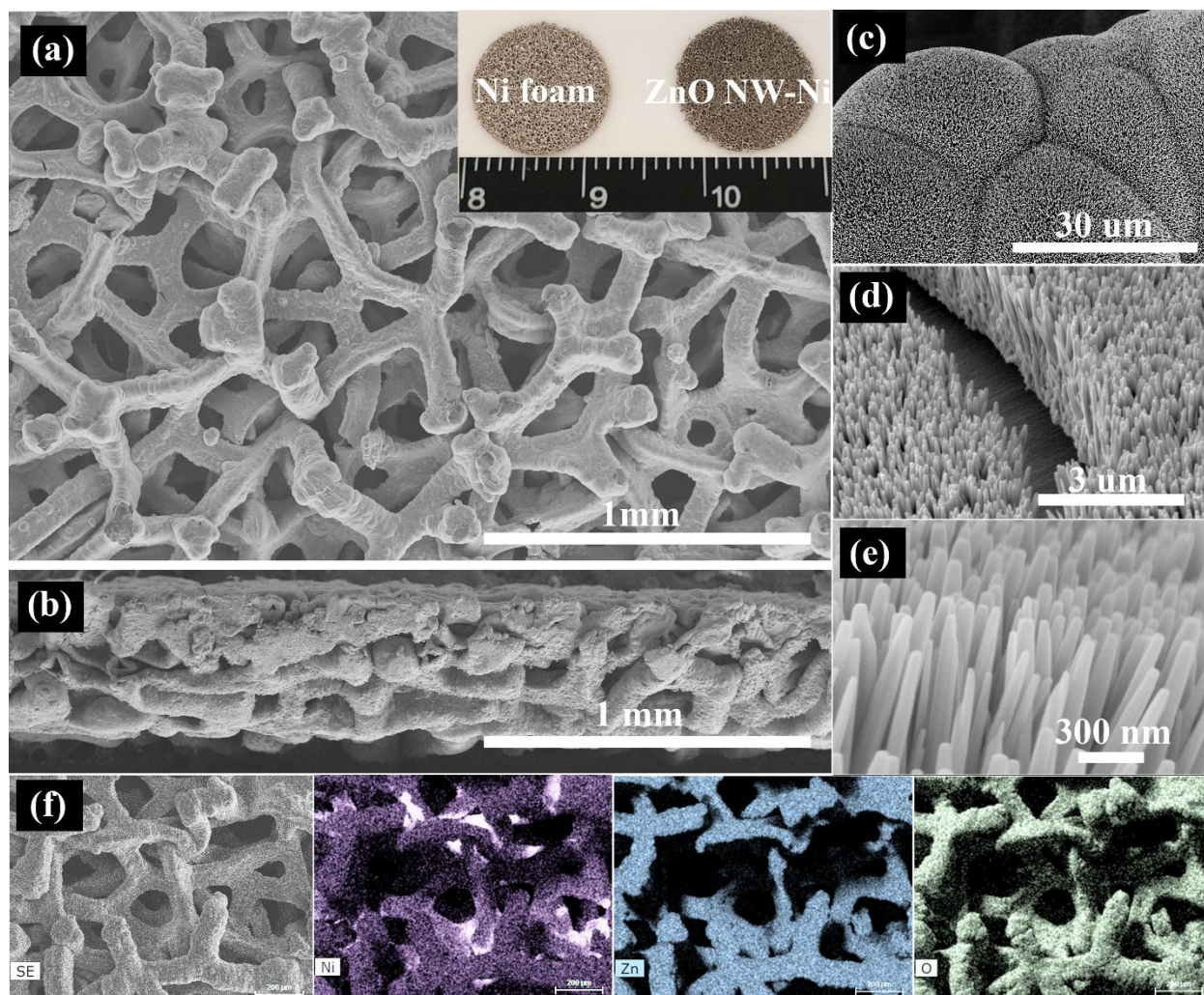


Figure 4.9: Top-View (a) And (b) Cross-Section Low Magnification SEM Images of the Hybrid ZnO Nanowires/Ni Foam Interlayer; (c-e) High-Magnification SEM Images of the Hybrid ZnO Nanowires /Ni Foam Interlayer; (f) Secondary Electrons (SE) SEM Image of The Hybrid ZnO/Ni Interlayer and the Corresponding Elemental Maps.

4.3.3 Zinc Oxide/Carbon Interlayer

To maximize the energy density of the batteries, the interlayer, which lies on top of the cathode, should be as light as in weight possible. Considering their tightly interwoven architecture and tunable thickness, free-standing carbon nanofiber mats were chosen as another desirable substrates for ZnO growth and were prepared by electrospinning. Generally, polymeric fibers are first obtained, followed by a facile thermal treatment for carbonization^[183]. The diameter of electrospun carbon fibers ranges from nanometers to micrometers and can be easily tuned by varying the concentration of precursor. And the conductivity of the resulting fibers mainly depends on the carbonization temperature and the intrinsic properties of polymer precursor.

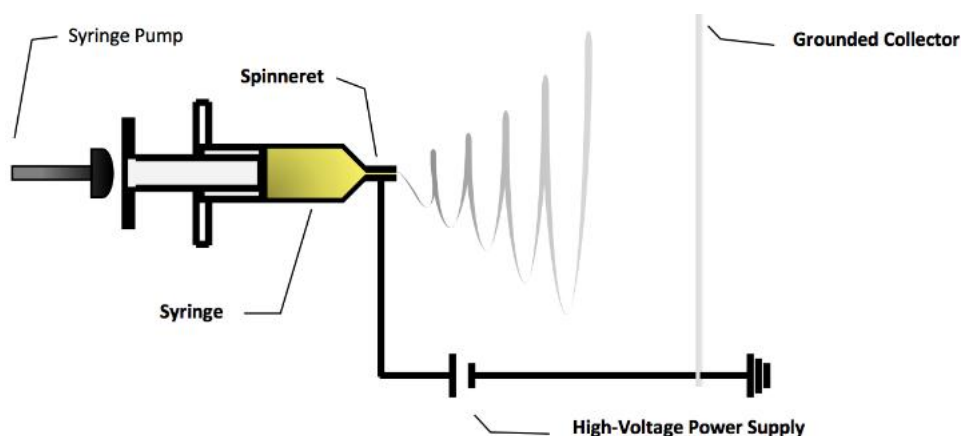


Figure 4.10: Schematic for the Set-up of Electrospinning.

In this study, commercial polyacrylonitrile (PAN) powder was used as the precursor due to its high carbon content and was dissolved in *N,N*-dimethylformamide (DMF) to form a solution. It was found that the solution concentration governs the diameter of electrospun PAN fiber. To get a carbon fiber mat with suitable surface area and mechanical strength, a solution containing 10 wt% PAN was prepared. The set-up of electrospinning is shown in **Figure 4.10**. Briefly, it consists of three parts: a high voltage supplier, a spinneret and a grounded conducting collector. During electrospinning process, a voltage of 20 kV was applied to the needle of the syringe and drops of polymer was pushed out continuously at a speed of 1 mL h⁻¹. Affected by the strong electrical field, the charged droplet on the needle tip elongated to form a Taylor cone and was rejected when repulsive electrostatic force overcame surface tension. The rejected droplet has an unstable electrohydrodynamic whipping motion between the tip and collector, during which solvent is evaporated and the droplet is further stretched to form fibers. Finally, the electro-spun PAN fibers were collected on Al foil collector after 2hs.

The obtained PAN fibers with a linear molecular chain were stabilized in air in order to maintain their fibrous structure and prevent shrinkage in subsequent carbonization. Stabilization process usually involves cyclization, dehydration and oxygen uptake, which is accompanied with the color change of fiber from white to brown (**Figure 4.11**). The stabilized PAN fibers have an aromatic ladder structure and contain about 50~60 wt% carbon. To further remove the non-carbon elements and increase the conductivity of fiber, the stabilized PAN fibers was carbonized at 1000 °C in an inert N₂ atmosphere containing 10 ppm O₂ for 6hs. Duration carbonization, the aromatic ladder structure of stabilized PAN was further converted to turbostratic graphite structure and finally a flexible black mat was obtained, whose size ($\sim 5.8 \text{ cm}^2$) was smaller than that of the precursor ($\sim 14 \text{ cm}^2$). (**Figure 4.12**)

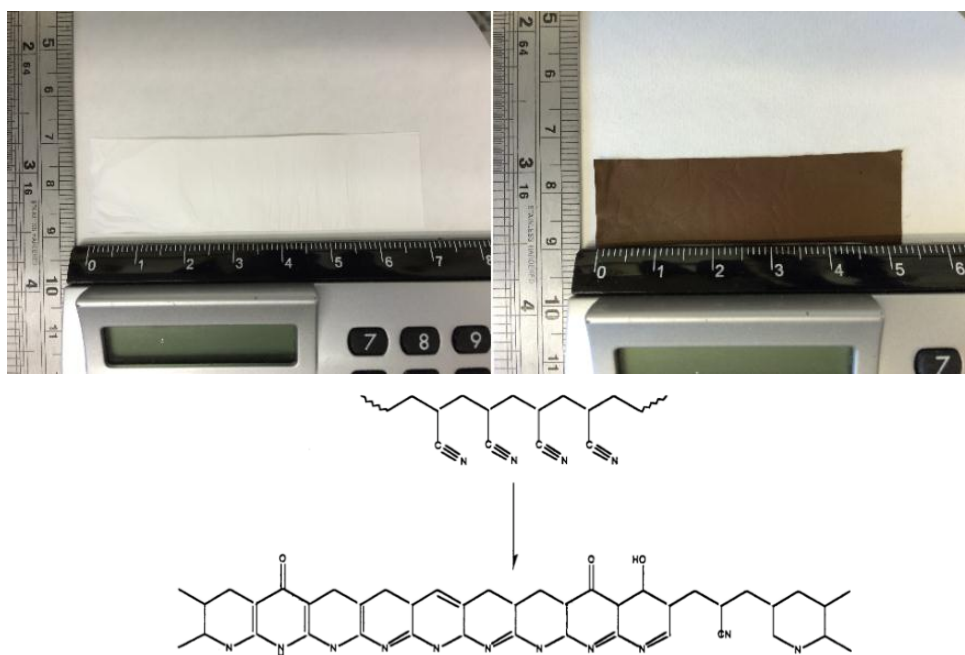


Figure 4.11: Photographs of PAN Precursor (White) and Stabilized PAN (Brown); The Structure Conversion of PAN During Stabilization Process.

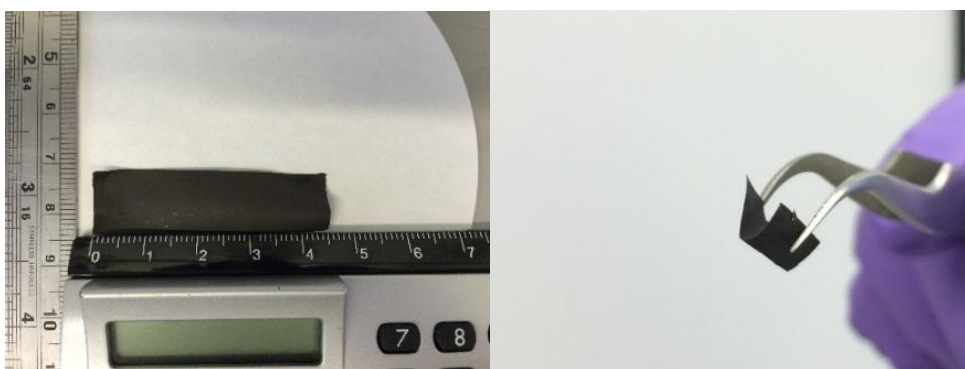


Figure 4.12: Photographs of Carbonized PAN Nanofiber Mats.

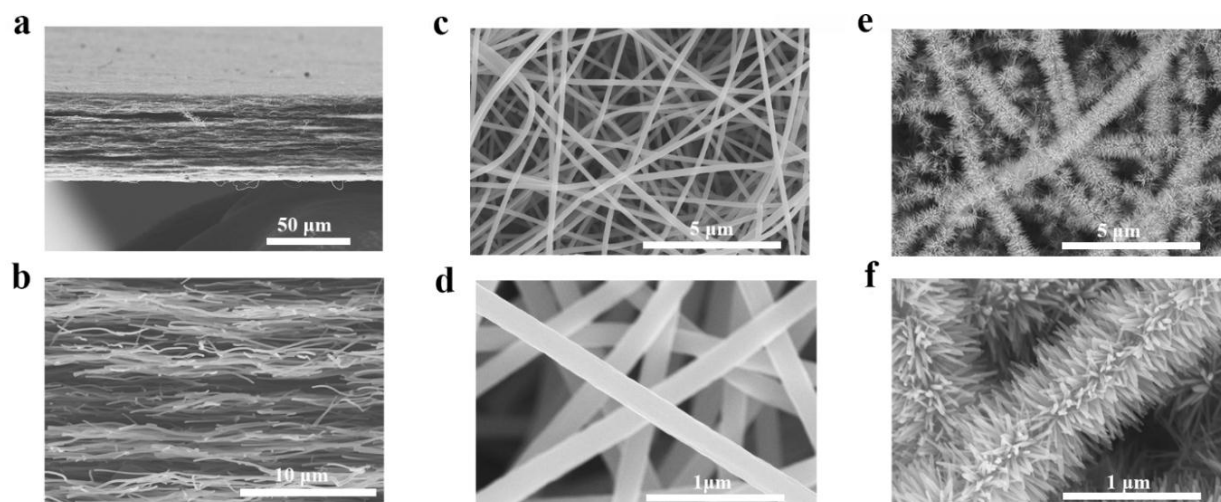


Figure 4.13: (a, b) Cross-Section of Low and High Magnification SEM Images of the Carbon Nanofiber Interlayer. Top-View Low and High Magnification SEM Images: (c,d) The Carbon Nanofiber Interlayer; (e,f) The Hybrid ZnO Nanowires/C Nanofiber Interlayer.

Figure 4.13a and 4.13b show the cross-section SEM images of the as-prepared carbon nanofiber mats. A layered structure with a thickness of approximately 50 μm is observed and the space between these loosely stacked layers is favorable for the infiltration of ZnO growth solution. From the SEM images shown in **Figure 4.13c and 4.13d**, it can be seen that the black carbon mat has a fish-net micro-structure formed by the interconnection of individual carbon nanofiber with an average diameter of 200 nm. After the uniform growth of ZnO nanowires on each carbon nanofiber, a fluffy and brush like architecture was achieved (**Figure 4.13e**). From a closer observation, the decorated ZnO nanowire has a diameter of ~ 50 nm and a length of ~ 500 nm (**Figure 4.13f**).

N_2 adsorption measurement was carried out to investigate the specific area and pore size and pore volume of C and ZnO/C nanofiber samples. Both of the nitrogen adsorption isotherms of C and ZnO/C nanofiber had a steep uptake of nitrogen molecules at a low relative pressure ($P/P_0 < 0.1$), corresponding to a type I behavior given by microporous solids. In fact, the C nanofiber with an average pore diameter of 2.37 nm had a dual pore structure. The mesopore inside the backbone of carbon fiber might be generated because of the removal of non-carbon elements and the reaction between carbon and low concentration O_2 to form CO gas during carbonization. The introduction of ZnO nanowires indeed affected the texture of C nanofiber, including the pore size, pore volume and BET specific area. It caused a decrease in the BET specific area of carbon from 600 m^2/g to 192 $\text{m}^2 \text{g}^{-1}$ due to the very small specific area of ZnO nanowires (**Figure 4.14**). Meanwhile, the pore volume was also reduced from 0.36 $\text{cm}^3 \text{g}^{-1}$ to 0.28 $\text{cm}^3 \text{g}^{-1}$, which was accompanied with the change of pore size from 2.37 nm to 5.86 nm. The ZnO nanowires was grown on a nanocrystal

seeds film coated on carbon nanofiber. This thin layer might fill some nanopores on the external surface of C nanofiber and prevent the adsorption of N_2 in the internal pores, leading to the aforementioned phenomenon.

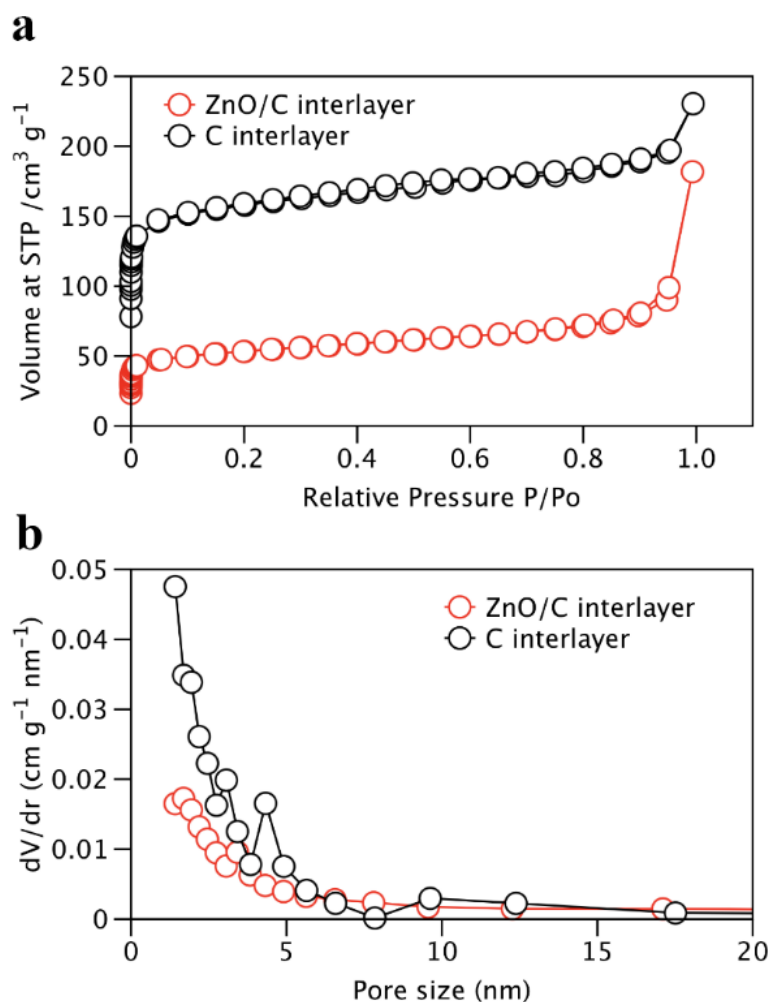


Figure 4.14: (a) Nitrogen Adsorption Isotherms and (b) Pore Size Distribution of ZnO Nanowire/Carbon Nanofiber Interlayer and Carbon Nanofiber.

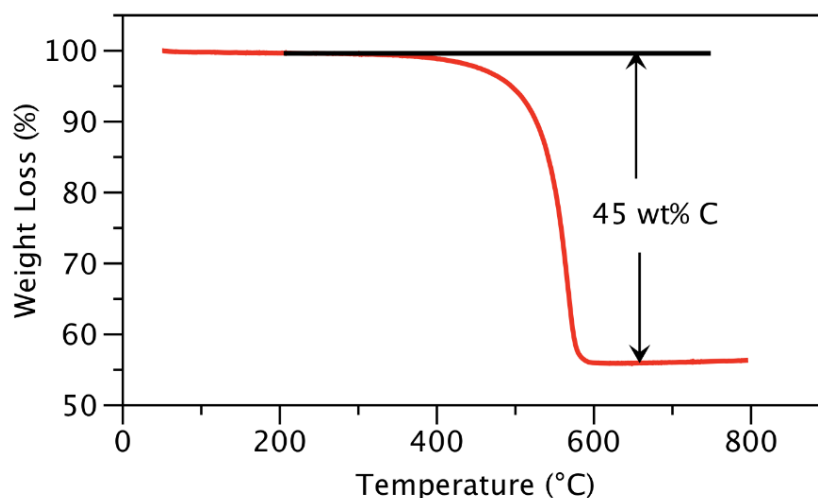


Figure 4.15: TGA Curves of ZnO Nanowires/Carbon Nanofiber Interlayer.

To ensure the uniform growth of ZnO on C nanofiber without adding too much weight, the length of ZnO nanowires was controlled at around 500 nm with an aspect ratio (the width to length) of 1:10. The total mass of ZnO/C interlayer was round 1.3 mg cm^{-1} . **Figure 4.15** shows the TGA curve of ZnO/C interlayer. The rapid mass loss during the temperature region of 400-600 °C is due to the combustion of carbon in air atmosphere. The content of ZnO in the hybrid interlayer was determined to be 55 wt%, corresponding to an areal loading of 0.7 mg cm^{-1} .

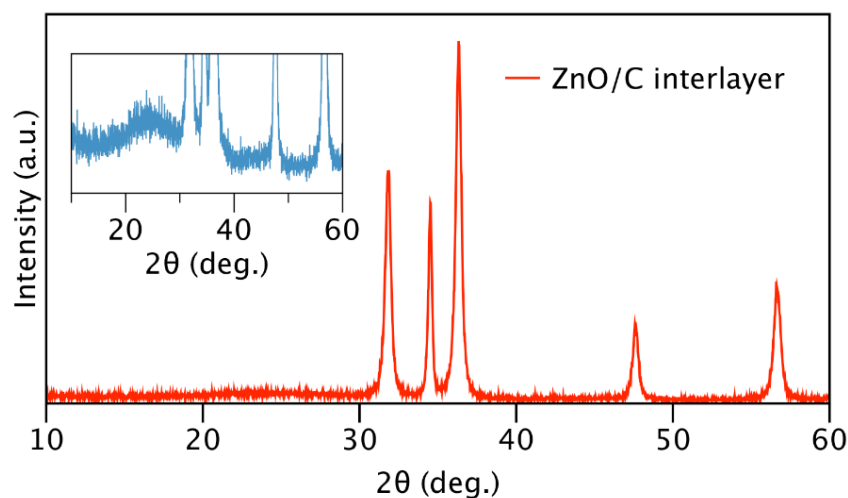


Figure 4.16: XRD Spectrum of ZnO Nanowire/Carbon Nanofiber Interlayer.

In addition, the crystal structure of ZnO/C interlayer was investigated by XRD. The sharp peaks were indexed to the hexagonal wurtzite phase of ZnO, which had no specific growth orientation due to the large curvature of carbon nanofiber. A small and broad peak was observed around $2\theta = 26^\circ$, indicating the PAN derived carbon nanofiber had an amorphous structure (**Figure 4.16**).

4.4 Electrochemical Test and Postmortem Analysis

4.4.1 A Proof of Concept

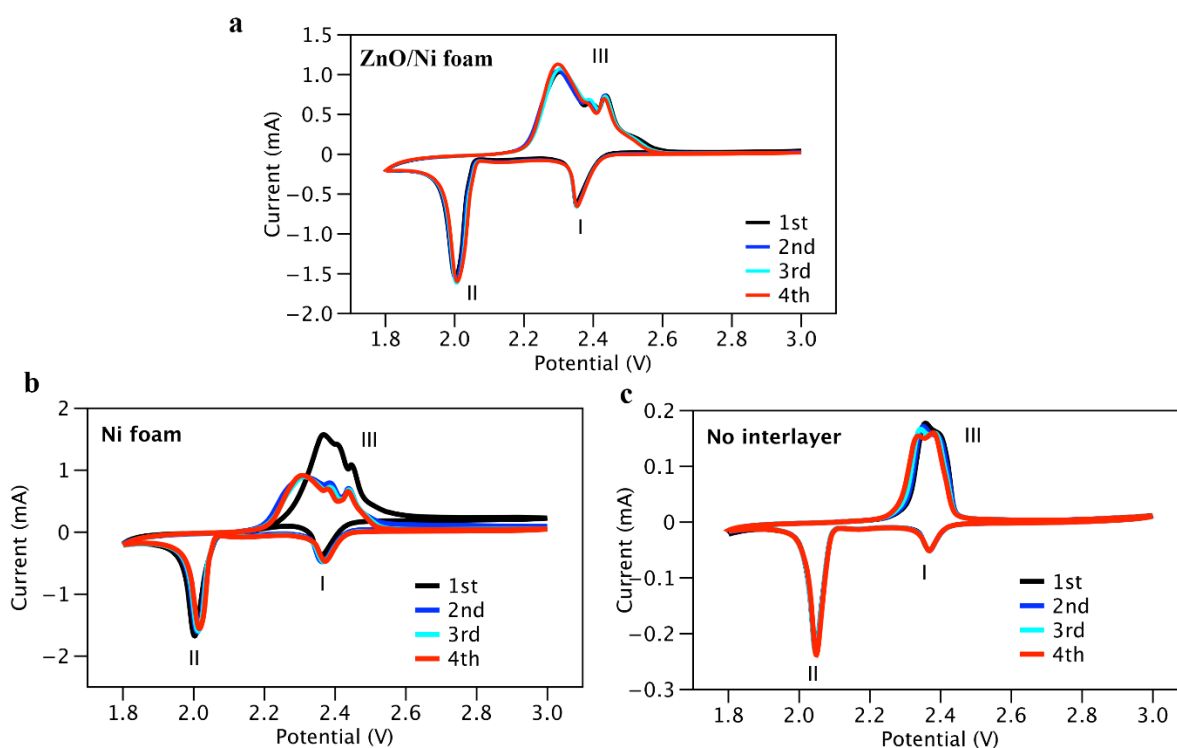


Figure 4.17: CV Plots of the Li-S Cell with Different Interlayers: (a) ZnO Nanowires/Ni Foam; (b) Ni Foam; (c) No Interlayer.

The effects of the hybrid ZnO nanowires/Ni foam interlayer on the electrochemical performance of the Li-S cell were investigated by comparison with a Li-S cell with bare Ni foam and without any sandwiched interlayer. The ZnO nanowires/Ni foam interlayer contributed to enhanced electrochemical reversibility. As shown in **Figure 4.17a-c**, all the cyclic voltammetry (CV) curves of S/MWCNT cathode with three different interlayers exhibited two reduction peaks at cathodic scan and one overlapped oxidation peak at anodic scan, which are typical electrochemical behavior of sulfur. Specifically, the small reduction peak at ~2.4 V (Peak I) is attributed to the conversion of cyclo-S to long-chain polysulfide (Li_2S_n , $4 \leq n < 8$) while the prominent peak at ~2.1 V (Peak II) corresponds to further reduction to lithium sulfide (Li_2S), which makes a major contribution to the overall capacity. The overlapped oxidation peak at 2.4 V (Peak III) is associated with the delithiation of Li_2S to sulfur.

Interestingly, there were some changes in the redox peaks induced by the Ni foam based interlayer. Both the redox current of cathodes with Ni foam based interlayer were increased, indicating that Ni foam based interlayers can provide extra conductive surface and enhance the electrochemical utilization of sulfur. In addition, the oxidation peaks of cathodes with Ni foam based interlayer were broader than that of cathodes without interlayer. It implies that the sulfur species can migrate to the surface of Ni foam based interlayer and undergo a relatively more complicated oxidation process. One reason for the peak-broadening phenomena might be the adsorption of intermediate sulfur species on Ni foam based interlayer. In addition, there was an obvious redox current decay after the 1st cycle scan for cathode with Ni foam interlayer, showing the poor confinement of sulfur species by Ni foam. In the case of cathode with ZnO nanowires/Ni foam interlayer, it should be noted that the position and intensity of these redox peaks show minimal changes with increasing scans, confirming a better electrochemical stability of the S/MWCNT cathode when sandwiched with this hybrid interlayer.

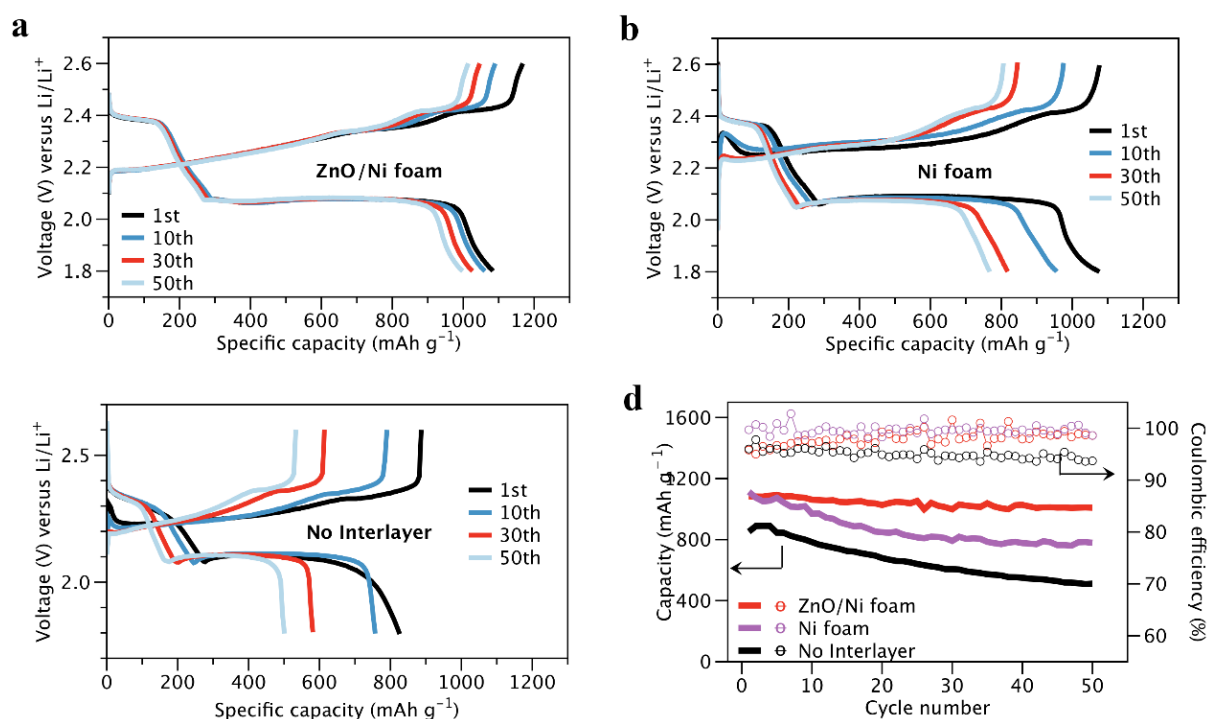


Figure 4.18: Discharge–Charge Profiles of the Li-S Cell with Different Interlayers after Different Cycles at 0.2C: (a) ZnO/Ni Foam; (b) Ni Foam; (c) No Interlayer; (d) Comparison of Cycle Performance of S/MWCNT Cathode with Different interlayers at a Current Density of 0.2C within a Potential Window of 1.8-2.6 V Versus Li/Li^+ for 50 Cycles.

The hybrid layer led to stable cycle performance. **Figure 4.18a-c** shows the discharge-charge profiles of the S/MWCNT cathode with ZnO nanowires/Ni foam interlayer after different cycles at a current density of 0.2C (1C=1672 mA/g). The distinct two-plateau discharge behaviour, which agrees well with CV results, was observed and remained unchanged during cycling. It reached an initial discharge capacity of 1088.5 mAh g⁻¹, corresponding to a S utilization of 65.1%. After 50 cycles, a reversible capacity remained high at 1009.1 mAh g⁻¹ with a capacity retention of 92.7%. In controlled experiments, S/MWCNT cathode with Ni foam exhibited a similar value (66.5%) of S utilization for the first cycle, whereas the one without the sandwiched layer had only 49.4% S utilization. In addition, both of these suffered from severe capacity decay attributed to the diffusion and dissolution of polysulfide in the electrolyte. The reversible capacity of these two cathodes after 50 cycles was only 779 and 511 mAh g⁻¹, corresponding to a capacity retention of 70% and 62%, respectively. Meanwhile, the average Coulombic efficiency of cathodes with Ni based layers over 50 cycles can reach almost 100%, which is approximately 5% higher than that of pure S/MWCNT cathode (**Figure 4.18d**). Thus, it is clear that the simple incorporation of a Ni foam has some beneficial effect for improving S utilization and Coulombic efficiency during cycling. According to the previous report, Ni can catalyze the polysulfides redox reactions due to its intrinsic surface chemistry^[184]. And the macroporous structure of Ni foam further ensures the electrocatalysis surface accessibility, but the polysulfides anchoring strength on Ni is not very strong, still leading to some capacity decay during charging and discharging. As soon as the Ni foam surfaces are modified with high surface area ZnO brush-like nanowire arrays, there is a dramatic improvement in cycle life performance.

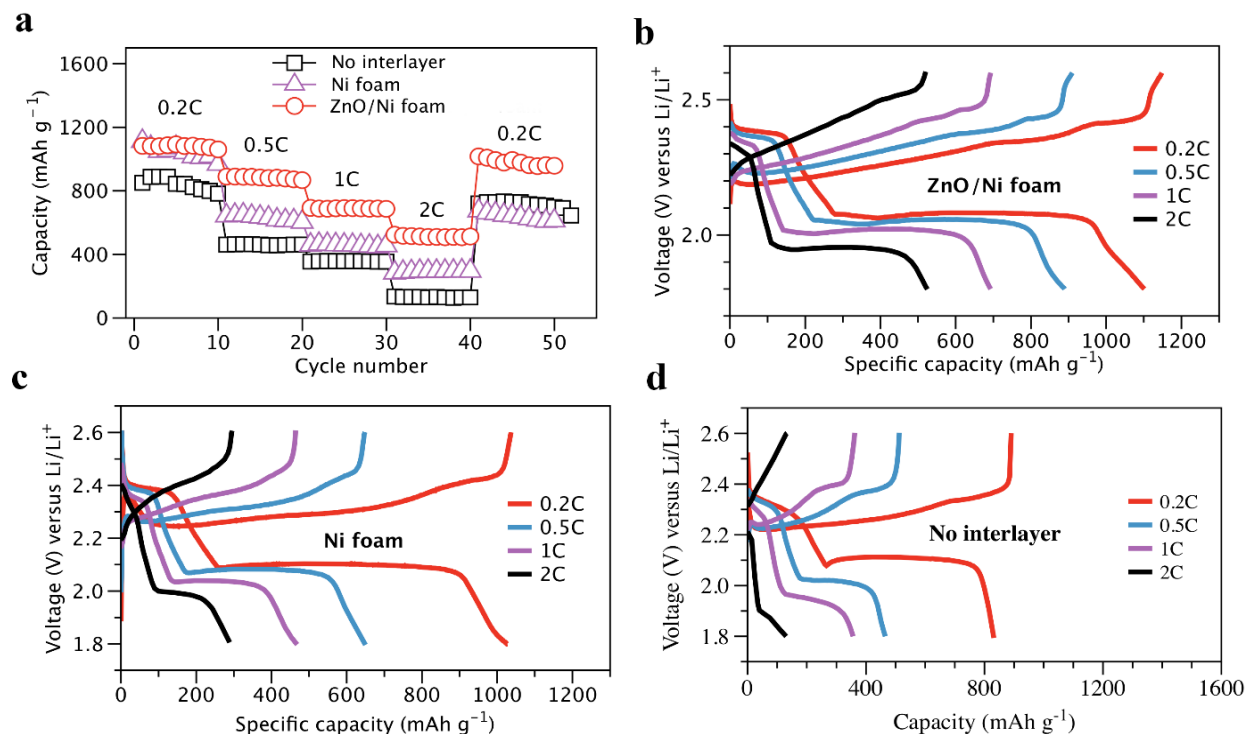


Figure 4.19: (a) Comparison of Rate Performance of Li-S Cell with Different Interlayers at Different Current Rates; (b) Nyquist Plots of Li-S Cell with Different Interlayers Measured Before Cycling.

The hybrid interlayer enabled good rate capability. **Figure 4.19a** compares the rate performance of S/MWCNT cathodes with different interlayers at a step-wise current rate from 0.2 to 2C and then back to 0.2C. After the first 10 cycles at 0.2C, the capacity of S/MWCNT cathodes with ZnO nanowires/Ni foam interlayer was maintained at 1073.6 mAh g⁻¹, which was gradually reduced to 867.6 mAh g⁻¹ and eventually to 687.3 mAh g⁻¹ at the end of each tenth-cycle testing at 0.5C and 1C, respectively. Remarkably, this structure can even deliver an average capacity of 513 mAh g⁻¹ at 2C and recover to a reversible capacity of 1017.3 mAh g⁻¹ when the current rate returned to 0.2C. The cathode with a Ni foam interlayer exhibited a similar capacity of 969.2 mAh g⁻¹ at the end of the initial 10 cycles, but there was an obvious capacity drop by 34% when the current rate suddenly increased from 0.2C to 0.5C. The reversible capacity at the end of tenth-cycle testing at 0.5, 1 and 2C was 604.8, 456.6 and 296.3 mAh g⁻¹, respectively, which were a little better than that of the cathode without any interlayer.

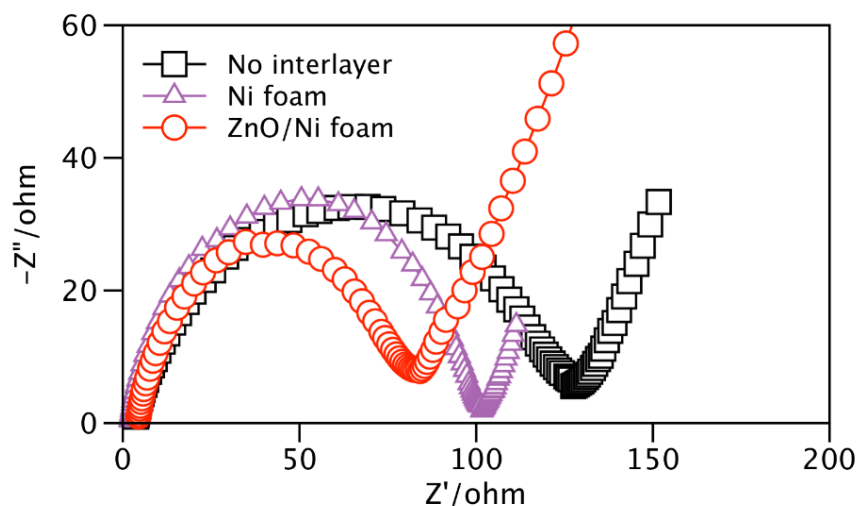


Figure 4.20: Nyquist Plots of Li-S Cell with Different Layers Measured before Cycling.

Figure 4.19b-d display the corresponding discharge-charge profiles of the S/MWCNT cathode with different interlayers at current rates ranging from 0.2 C to 2C. Compared with the other two cathodes, the one with the incorporation of ZnO nanowires/Ni foam interlayer exhibited much better rate tolerance, with little change in plateau potential at various rates. The superior rate performance of the S/MWCNT cathode with the hybrid interlayer compared to that of controlled experiments can be attributed to its relatively low electron transfer resistance (R_{ct}) as evidenced by Electrochemical Impedance spectroscopy (EIS) (**Figure 4.20**). Although ZnO is a semiconductor with a band gap of 3.37 eV, its dense brush-like structure on the surface of Ni foam can act as bridges between Ni foam and cathode and provide parallel and efficient ways for electron transfer, thus reducing the interfacial resistance. More importantly, the surface charges of ZnO nanowires might be mobile at the open potential of 3V, leading to good connectivity.

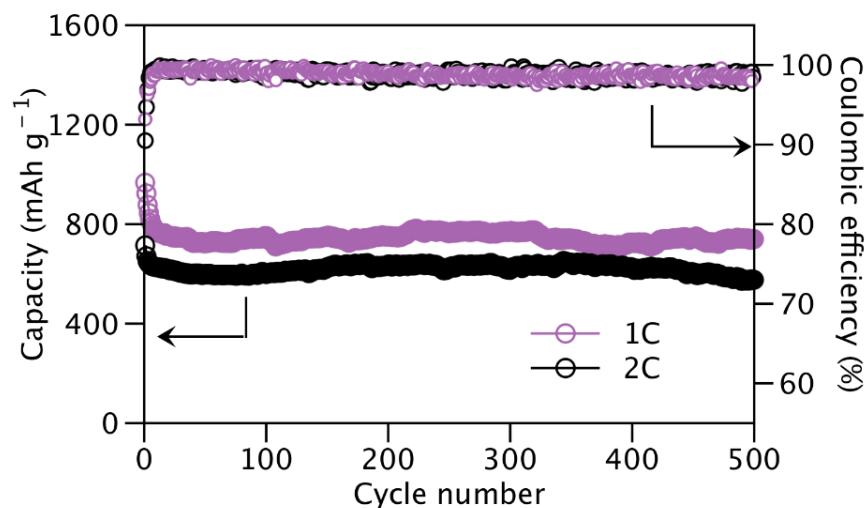


Figure 4.21: Cycle Performance of the Li-S Cell with ZnO Nanowires/Ni Foam Layer at High Current Rates.

The ultra-long cycle performance of S/MWCNT cathodes with ZnO nanowires/Ni foam interlayer at high rates is plotted in **Figure 4.21**. At a current rate of 1C, a reversible capacity of 740.5 mAh g^{-1} with a capacity retention of 77% is achieved after 500 cycles. When the current rate increased to 2C, the cycling capacity dropped slightly to 577.1 mAh g^{-1} and the capacity retention was increased to 81% because of the limited dissolution of polysulfides in organic electrolyte at high current rate.

To understand the reason behind the remarkable electrochemical performance, the hybrid ZnO nanowires/Ni layer was recovered from the fully charged coin cell after 500 deep cycles at 2C and its morphology was characterised by SEM and TEM. It was found that ZnO nanowires played a key role in chemically capturing S species. As shown in the elemental EDS maps in **Figure 4.22a**, a uniformly distributed S signal was detected on the cycled ZnO nanowires/Ni layer, which provides direct evidence for the migration and adsorption of active material from the MWCNT host to the ZnO nanowires/Ni interlayer during cycling. From a closer observation (**Figure 4.22a, inset**), the 1D nano architecture of ZnO has survived intact on the Ni foam even after 500 deep cycles and a new fairly rough layer was coated on each nanowire to form a core-shell structure. From the TEM images in **Figure 4.22b-c**, the average thickness of the coating shell was approximately 30 nm; EDS mapping also confirms this shell as S-containing species anchored on the surface of ZnO nanowires.

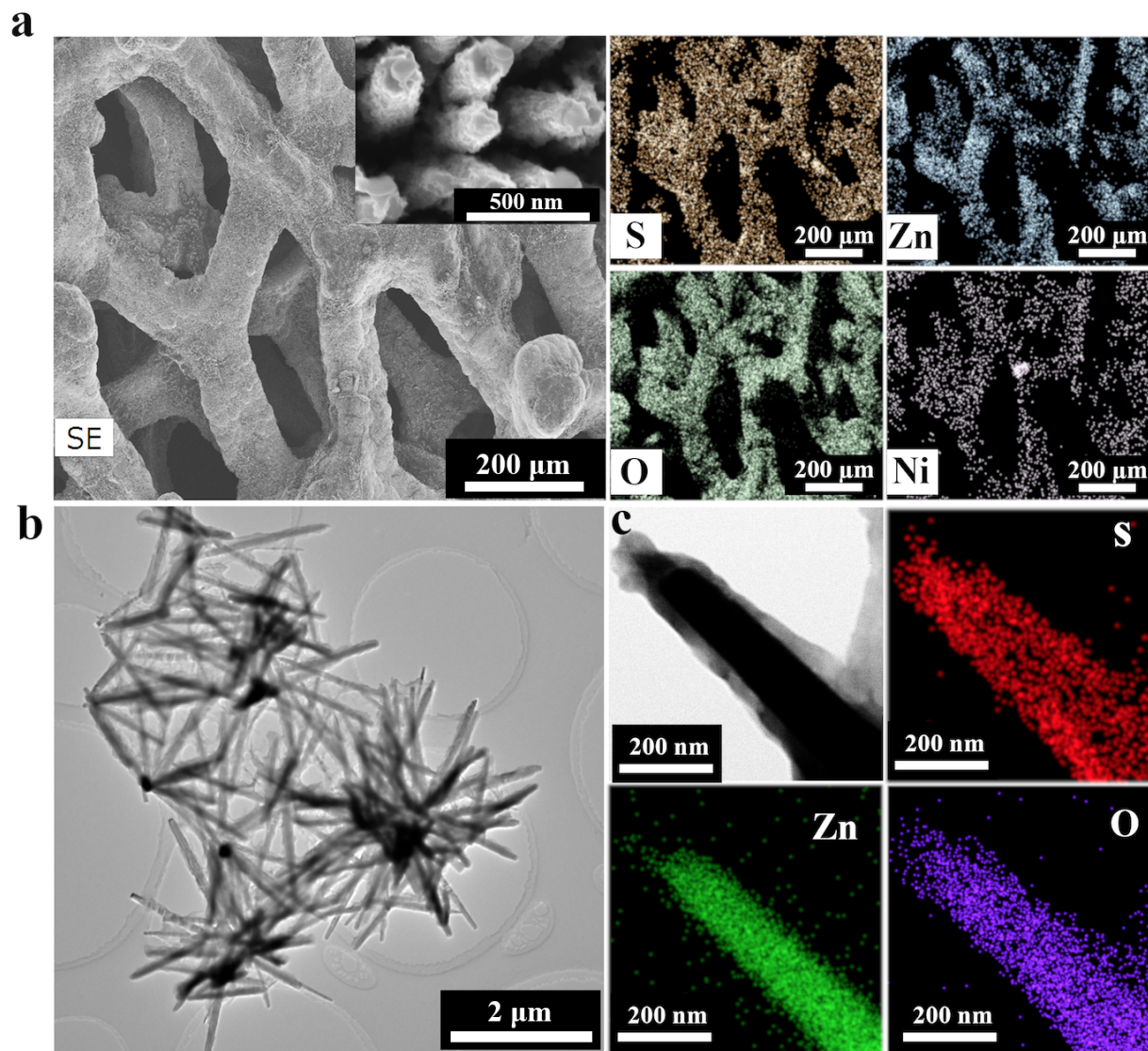


Figure 4.22: (a) Low Magnification SEM Image of the Cycled Hybrid Interlayer and Corresponding Elemental Mappings (Inset: High Magnification SEM Image); (b) TEM Image of Cycled ZnO Nanowires; (c) TEM Image of A Single ZnO Nanowire with a Rough S-Containing Shell and Corresponding Elemental Maps.

The chemical composition of S species was investigated by X-ray photoelectron spectroscopy (XPS). **Figure 4.23a** compares the XPS survey spectra of the ZnO nanowires/Ni foam interlayer before and after cycling. The intensity of Zn signals from ZnO was markedly reduced with the appearance of S signal in the spectrum after cycling, which agrees well with the coating of S species on the ZnO surface. No other signals such as F, N, were detected in the surveyed spectrum of the cycled hybrid interlayer, which indicates that electrolyte salt was completely removed from the robust structure of the cycled ZnO nanowires/Ni foam interlayer after an intense and a thorough wash and the observed S signals mainly arise from the migrated active materials.

Figure 4.23b show the S 2p XPS spectra of the cycled hybrid interlayer. It can be seen that four S-containing species were identified, including Li_2S_2 (162.6 eV, 162.1 eV), S_8 (164.1 eV, 163.2 eV), thiosulfate (167.2 eV) and polythionate complex (169.7 eV, 168.7 eV). The deposition of discharge product Li_2S_2 cannot be avoided due to its insulating nature and poor electrochemical reversibility. Because of the lower redox potential of ZnO than that of polysulfides, the generated thiosulfate/polythionate complex could mainly come from the oxidation of polysulfides by LiNO_3 , which is a common additive in the electrolyte to somewhat mitigate the polysulfides shuttle effect^[62, 88]. Except S_8 , other S-containing species cannot be electrochemically reutilized, but thiosulfate and polythionate can act as a polysulfide mediator to chemically curtail active loss during charge and discharge process. **Figure 4.23c** compares the Zn 2p_{3/2} XPS spectra of ZnO/C interlayer before and after cycle. It can be seen that a slight binding energy shift of Zn 2p_{3/2} from 1021 eV to 1020.5 eV after cycling was observed, reflecting the chemical interaction between ZnO and S species.

To give further insight into the chemical confining effect of ZnO on polysulfides, the binding energy (E_b) of five most relevant S species (Li_2S_n) on the polar O-terminated surface of ZnO was calculated using density functional theory (DFT) because the strong binding of metal oxide and lithium polysulfides mainly originates from Li-O interaction according to the previous report^[155]. As shown in **Figure 4.23d**, the E_b value for Li_2S_8 remarkably reaches 3.98 eV, which is one the highest reported for similar systems^[185]. With a decrease in molecular length of polysulfides, the corresponding E_b reduces to a lowest value of 1.26 eV for Li_2S_4 due to the limited interaction area. After that, E_b gradually increases to 2.70 eV for Li_2S , which could be explained by the enhanced interaction between the O-terminated surface and short-chain polysulfides due to similar polarity.

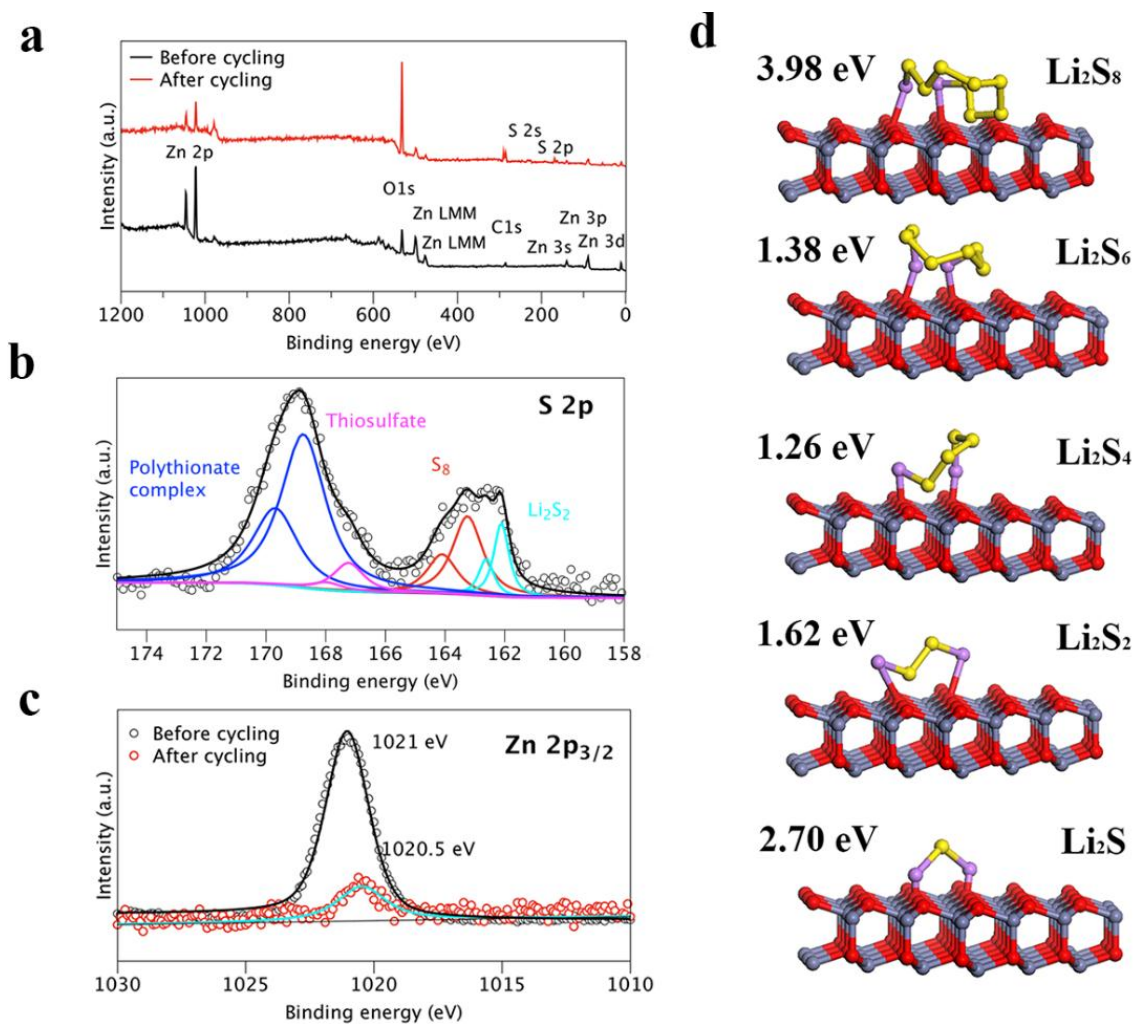


Figure 4.23: (a) XPS Survey Spectra of Hybrid Layer before and after Cycling; (b) S2p XPS Spectrum of the Cycled Hybrid Layer; (c) Comparison of Zn 2p_{3/2} XPS Spectrum of the Hybrid Layer before and after Cycling; (d) Optimized Configurations for the Binding of Five S Species to The O-Terminated Polar Surface of Wurtzite ZnO Crystal.

4.4.2 A Light-Weight Battery

Once the concept of polysulfide adsorptive brush is proven, the next task is to replace the high density Ni foam with a light, porous material to reduce the overall weight of batteries. The effects of the hybrid ZnO/C interlayer on the electrochemical performance of Li-S cell were investigated using S/MWCNT composite as cathode and Li as anode. To ensure the same sulfur content considering the combined mass of cathode and interlayer, a S/MWCNT composite cathode with a $\sim 110\ \mu\text{m}$ -thick carbon nanofiber interlayer was tested for reference.

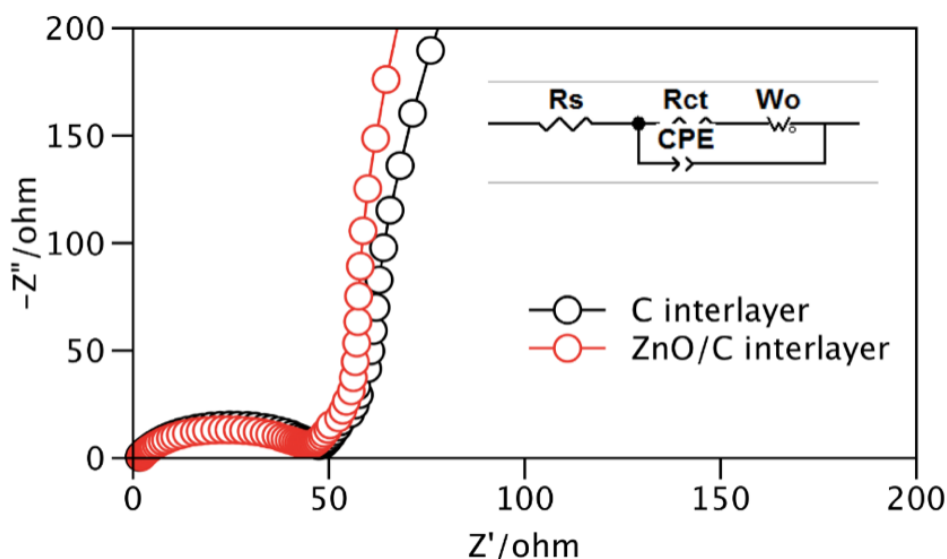


Figure 4.24: Nyquist Plots and the Equivalent Circuit (Inset) for the S/MWCNT Composite Cathode with Different Interlayers.

Initially, electrochemical impedance was measured at open circuit potential (OCP) of cells to characterize the internal resistance. The Nyquist plots of S/WMCNT composite cathode with different interlayers are displayed in **Figure 4.24**. Interestingly, it was found that both samples had a similar charge transfer resistance (R_{ct}) of approximately $45\ \Omega$, which could be attributed to the equivalent effect of introduction of semi-conducting ZnO and increase in the thickness on the conductivity of carbon nanofiber interlayer.

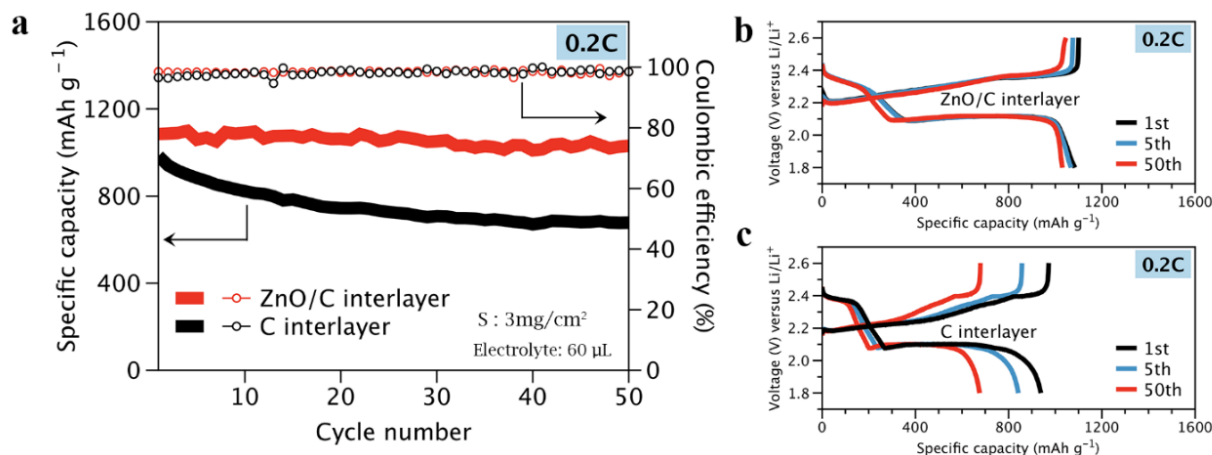


Figure 4.25: (a) Cycle Performance of the Li-S Cell with Different Interlayers at a Current Rate of 0.2C. Discharge–Charge Profiles of the Li-S Cell with Different Interlayer after Different Cycles at 0.2 C; (b) ZnO/C; (c) C Interlayer.

Figure 4.25 compares the cycle performance of S/MWCNT composite cathode with two different interlayers at a current rate of 0.2C. For S/MWCNT cathode with a ZnO/C interlayer, it reached an initial discharge capacity of 1084.7 mAh g⁻¹, corresponding to a S utilization of 64.8%. After 50 cycles, a reversible capacity remained high at 1030.7 mAh g⁻¹ with a capacity retention of 95%. In controlled experiment, S/MWCNT cathode with carbon nanofiber interlayer exhibited a slightly lower sulfur utilization (58.8%) for the first cycle, but its capacity retention after 50 cycles was only 68.8%. Thus, the hybrid ZnO/C interlayer led to better cycle performance. Figure 4b and 4c shows the discharge-charge profiles of S/MWCNT cathode with different interlayers in the 1st, 5th and 50th cycle, respectively. The distinct two-plateau discharge behavior was observed in all profiles, which is the typical electrochemical features of sulfur. At high and steep plateau around potential of 2.3V, cyclo-S₈ is converted to long-chain polysulfides Li₂S_n (4 < n < 8). As discharge proceeds onward, short-chain polysulfides Li₂S_n (2 < n < 4) and even solid Li₂S₂/Li₂S are formed at long and planar plateau around potential of 2.1V. Notably, S/MWCNT cathode with ZnO/C interlayer exhibited less potential hysteresis with cycling compared with the control sample.

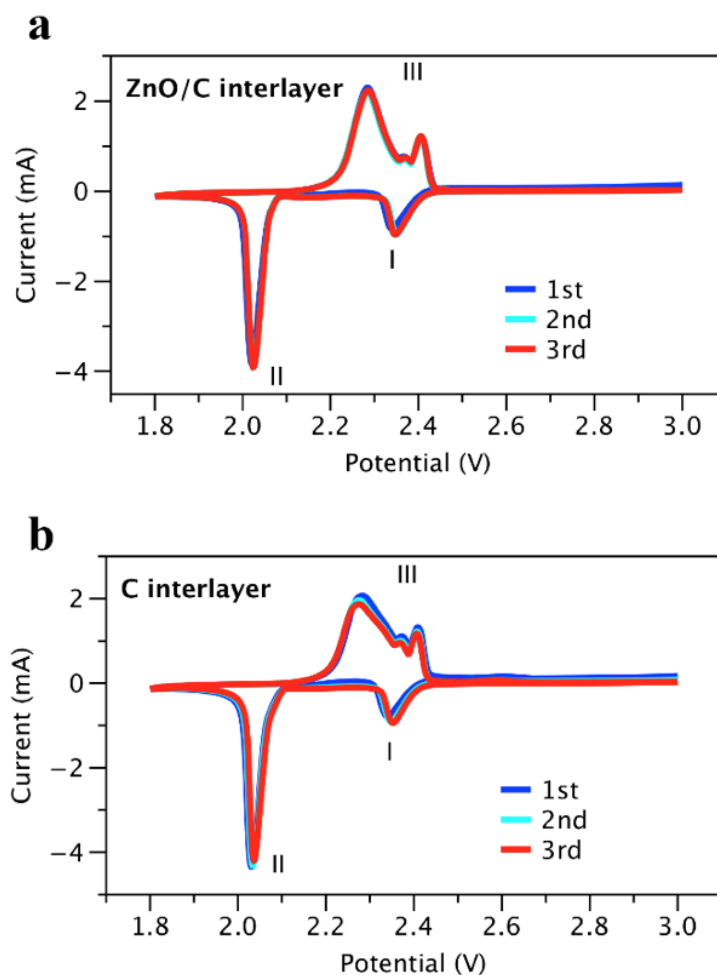


Figure 4.26: CV Curves of S/MWCNT Composite Cathodes with Different Interlayers at a Scan Rate of 0.1mV/s: (a) ZnO Nanowires/Carbon Nanofibers Interlayers; (b) Carbon Nanofibers Interlayers.

In addition, the position and intensity of redox peaks in the cyclic voltammetry (CV) curves of S/MWCNT cathode with ZnO/C interlayer also showed less changes during the first three cycles than that of S/MWCNT cathode with C interlayer, indicating an enhanced reversibility of S redox (**Figure 4.26**). Although the incorporation of interlayers for sulfur cathode led to a similar change in the shape of oxidation peaks, the width of the main peak around 2.27 V varies with the interlayer thickness. A thinner interlayer contributes to a faster oxidation process. The interlayer with a porous structure might serve as an electrolyte reservoir, which affects the diffusion distance of Li ion.

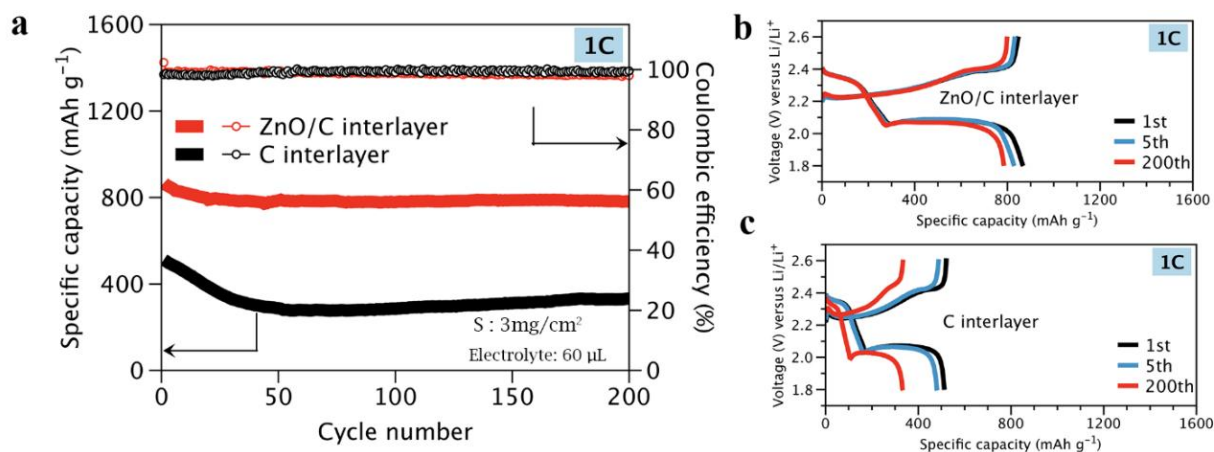


Figure 4.27: (a) Cycle Performance of the Li-S Cell with Different Interlayers at a Current Rate of 1C; Discharge–Charge Profiles of the Li-S Cell with Different Interlayer after Different Cycles at 1C; (b) ZnO/C; (c) C Interlayer.

The long cycle performance of S/MWCNT cathodes with two different interlayers at a high current rate of 1C is plotted in **Figure 4.27a**. Compared with the performance at 0.2C, reduced S utilization and capacity stability were observed for both samples during the initial 50 cycles at 1C. Generally, the utilization of sulfur mainly depends on two factors: (1) intimate contact with conductive framework; (2) effective confinement of soluble intermediate polysulfide. When it comes to a high current rate, kinetics of S redox and ion diffusion are also of great concern. S/MWCNT cathode with ZnO/C interlayer delivered an initial capacity of 867.6 mAh g⁻¹, which gradually reduced to 787.6 mAh g⁻¹ after 50 cycles with a capacity retention of 90.7%. After 200 cycles, a reversible capacity of 776 mAh g⁻¹ was achieved, corresponding to only 0.05% average capacity loss per cycle. In contrast, the initial capacity of S/MWCNT cathode with C interlayer at 1C was much lower (512.7 mAh g⁻¹), about 60% of that of S/MWCNT cathode with ZnO/C interlayer, followed by a rapid decay to 287.5 mAh g⁻¹ at 50 cycles. The corresponding capacity retention was 56%. With the slow infiltration of electrolyte in the thick C interlayer, the capacity gradually increased after 50 cycles and maintained at 333.5 mAh g⁻¹ after 200 cycles with 0.17% average capacity loss per cycle. **Figure 4.27b and 4.27c** display the discharge-charge profiles of the S/MWCNT cathode with different interlayers in the 1st, 5th and 200th cycle, respectively. It can be seen that the system with the incorporation of ZnO/C interlayer exhibited much better rate stability, with negligible change in plateau potential with cycling.

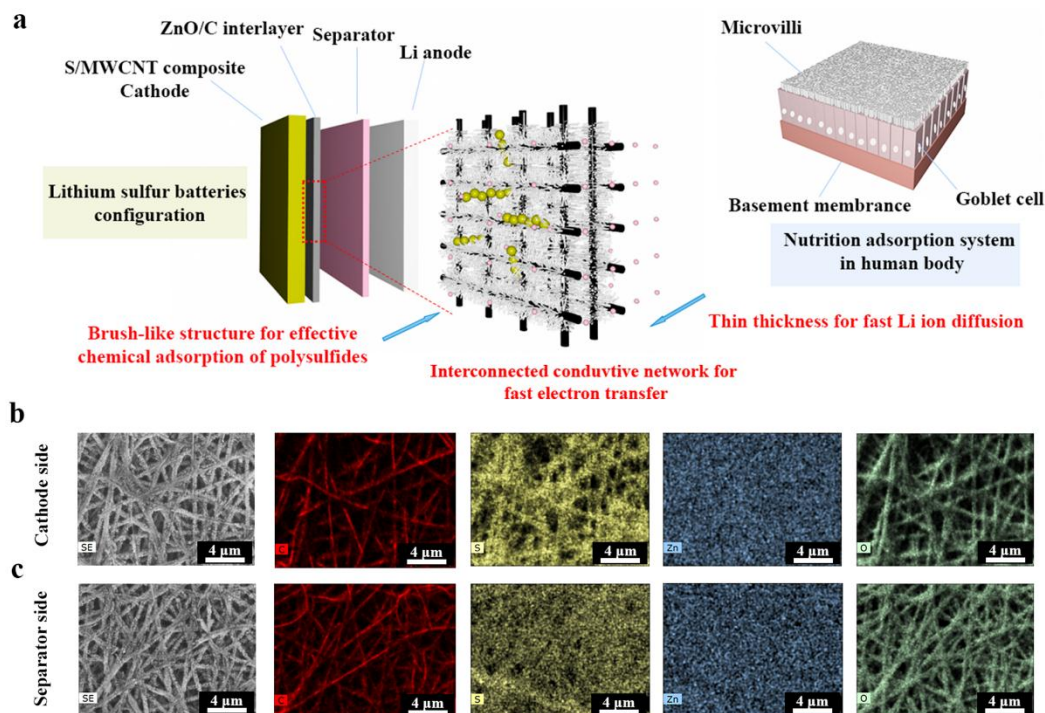


Figure 4.28: (a) Schematic of the Structural and Chemical Function of the Hybrid ZnO Nanowires/Carbon Nanofibers Interlayer in Li-S Batteries; SEM Image of the Cycled Hybrid ZnO Nanowires/Carbon Nanofibers Interlayer and Corresponding Elemental Map: (b) Cathode Side; (c) Separator Side.

The unique brush-like structure of ZnO/C interlayer mainly contributed to the superior electrochemical performance. As shown in **Figure 4.28a**, the self-organized zinc oxide nanowires forms a “brush border” on carbon nanofiber, which increases the contact area for electrolytes. And individual zinc oxide nanowire acts as “microvilli” to chemically adsorb the dissolved polysulfides in electrolytes. The whole capture process of migrating polysulfides mimics the adsorption of nutrients in intestinal cells. Meanwhile, the carbon nanofiber mat provides interconnected conductive network for reutilizing polysulfides and its thin thickness ensures trapping polysulfides without hampering lithium ion conductivity. To better understand the function of this brush-like ZnO/C interlayer, elemental distribution mapping on both sides of cycled ZnO/C interlayer after 200 cycles at 1C was conducted using EDS. As shown in **Figure 4.28b and 4.28c**, it can be seen that intense S signal were detected on the side facing cathode, directly evidencing that ZnO/C interlayer had the capability of anchoring and reutilizing migrating polysulfides. On the other hand, the S signal was weak on the side facing the separator. The semi-quantitative calculation of the amount of S anchored on the different sides of brush-like interlayer was carried out based on the corresponding EDS spectra shown in **Figure 4.29**. It was found the atomic ratio of S to Zn on the cathode side was about 5 times higher than that on the anode side, implying that most dissolved polysulfides were adsorbed by this thin interlayer.

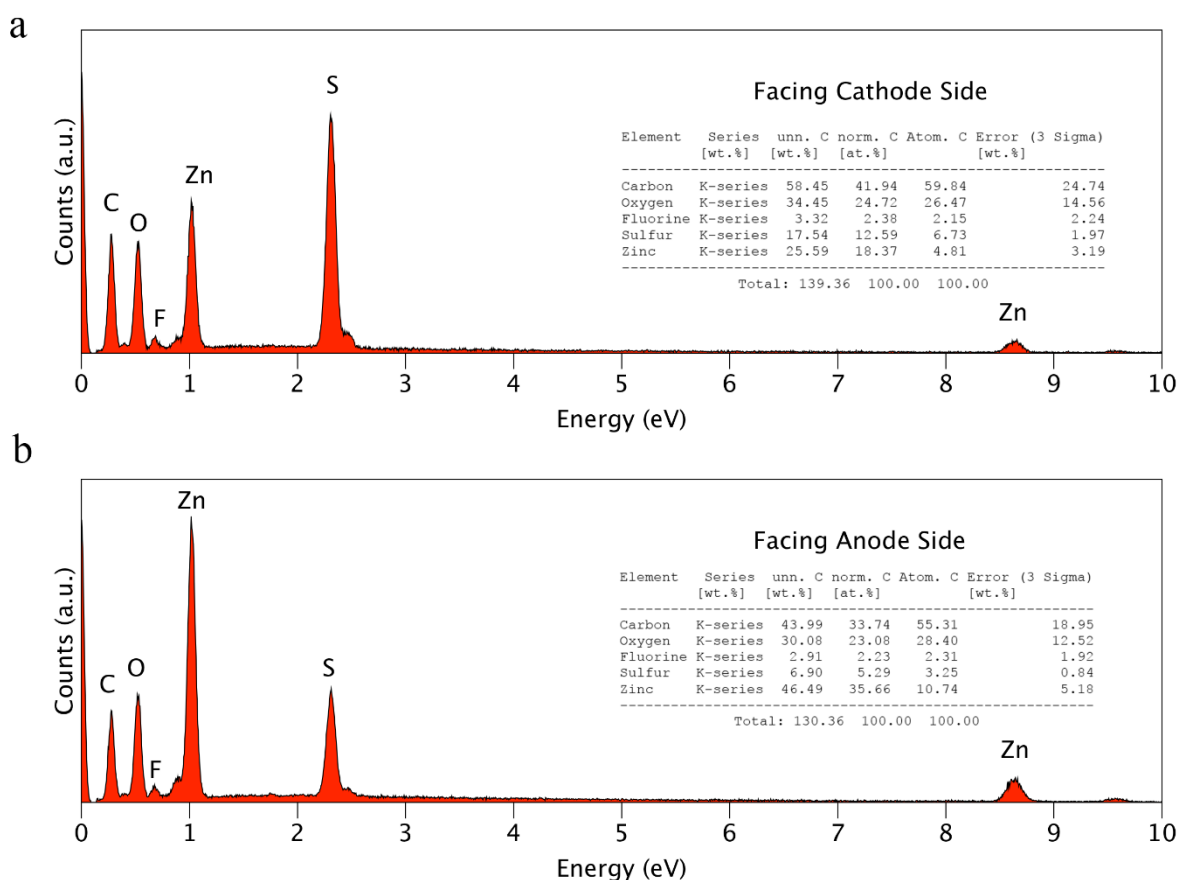


Figure 4.29: EDS Spectra for the Cycled ZnO/C Interlayer: (a) Facing Cathode Side; (b) Facing Anode Side.

4.5 Summary of this Chapter

In conclusion, a good cycle and rate performance of Li-S batteries has been demonstrated by using a zinc oxide nanowire based brush-like interlayer. ZnO nanowires play the key role in adsorbing migrating polysulfides due to a strong chemical bonding and their well-organized brush-like nano-architecture built on thin and interconnected conductive framework, which mimics the microstructure of intestinal cells, further enhances the effectiveness of polysulfides adsorption and reutilization process by affording fast electron and ion motion. Thanks to the bio-inspired ZnO/C interlayer, the S/MWCNT composite cathode with a high S loading of 3 mg cm^{-2} maintained a reversible capacity of 776 mAh g^{-1} after 200 cycles at 1C, corresponding a 0.05 % average capacity loss per cycle.

Chapter 5 A Praline-Like Flexible Interlayer with Highly Mounted Polysulfide Anchors for a Sulfur/Carbon Nanotube Cathode

5.1 Overview of the Work

In the previous chapter, functional brush-like interlayers were prepared by ex-situ growing zinc oxide nanowires onto different conductive substrates (Ni foam and carbon nanofiber) using a wet-chemistry method. The as-prepared interlayers successfully improved the batteries performance because of the high surface area of the brush-like structure and the strong chemical bond between ZnO with polysulfides. However, this nano design of interlayer has one drawback that the polysulfides adsorbed on the surface of ZnO nanowires might take a long diffusion path to the conductive substrate where the conversion reaction occurs. This may reduce the utilization efficiency. It would be better to develop an in-situ approach to load metal oxides not only outside but also inside the substrate in order to set a polysulfides diffusion gradient through the conductive framework.

In this chapter, a flexible praline-like interlayer comprised of titanium oxide (TiO_2) nanoparticles and carbon bonded together to form relatively long fibers was prepared by carbonizing an electrospun TiO_2 /PVP precursor. The structural morphology of the TiO_2 /C interlayer was characterized by different techniques to confirm the distribution of TiO_2 over the carbon backbone. The as-prepared interlayer was then placed on the surface of the previously used carbon nanotube/sulfur composite cathode to explore its effect on the electrochemical performance. To better understand it, the TiO_2 /C interlayer was recovered from the coin cell after cycling tests and its morphology was characterized by SEM and STEM. In addition, the chemical interaction of TiO_2 between S species was revealed by XPS and the theoretical calculation of binding energy using DFT theory. Finally, the formation mechanism of the praline-like structure of the interlayer was investigated by tuning the ratio of precursor components and carbonization temperature.

Parts of the findings are reported in Small:

T. Zhao, Y. Ye, C.Y. Lao, G. Divitini, P. R Coxon, X. Peng, X. He, H.K. Kim, K. Xi, C. Ducati, R. Chen, Y. Liu, S. Ramakrishna, R. V. Kumar, *Small*. **2017**, 13, 1700357

5.2 The Methods

5.2.1 Electrospinning of TiO₂-PVP Nanofiber Precursor

Firstly, a TiO₂ sol was prepared though adding Titanium (IV) isopropoxide (1mL) into ethanol (5 mL), which was stirred for 6 hours under ambient temperature followed by an additional acetic acid (2 mL, 8M). Polyvinylpyrrolidone (PVP, MW=1,300,000) of different concentration ranging from 0.03 g mL⁻¹ to 0.07 g mL⁻¹ was dissolved into 4 mL of ethanol. A further 18-hour stirring was required before mixing the two solutions. The total electrospun precursor was 12 mL. Then, the readily TiO₂ sol precursor was loaded into a syringe with a stainless steel nozzle for conventional electrospinning process. The applied voltage was set at 20 kV, and the ejection rate of precursor was 1.3 mL hr⁻¹. The as-spun nanofibers were collected with an aluminum foil located 15 cm away from the tip of the nozzle.

5.2.2 Carbonization of TiO₂-PVP Nanofiber Precursor

The peeled amorphous TiO₂ nanofiber precursor was transferred into a tube furnace and was sintered at temperature ranging from 800-1000 °C under a nitrogen atmosphere for 3 hours in order to crystallize TiO₂ and to carbonize PVP. The obtained TiO₂/C mat was then cut into small disk with a diameter of 11 mm and mass of 1.6 mg cm⁻².

5.2.3 Theoretical Calculation

The calculations were performed by using Predew-Burke-Ernzerhof functional with the Generalized Gradient Approximation method implemented in the Materials Studios. A 2×2×2 supercell was used to model the rutile-TiO₂ and was first cut to generate 110 surface. The vacuum slab crystal of the rutile-TiO₂ (110) with a vacuum thickness (VT) of 10Å was built. The geometry of the obtained model was first optimized with the ultrasoft pseudopotentials. The energy cutoff for the plane wave (PW) basis set was 340 eV and the k-point sampling was 5×5×8. All atoms were fully relaxed when the following convergence tolerance was met: the residual forces on the constituent atoms became smaller than 0.03 eV Å⁻¹ and the maximum atomic displacement was higher than 0.001 Å. The binding energy (Eb) of Li₂S_n on TiO₂ was calculated using the following equation: Eb=E(Li₂S_n)+E(TiO₂)-E(Li₂S_n/TiO₂).

5.3 Microstructure and Morphology Characterization

5.3.1 TiO₂/PVP Composite Precursor

Preparation of precursor solution is an important step for controlling the morphology and composition of electro-spun nanofiber. In this study, PVP was used as carbon source because of its good compatibility with Titanium (IV) isopropoxide, which is a common precursor for the preparation of homogeneous TiO₂ sol via a simple hydrolysis reactions^[186]. To further stabilize the sol and control the hydrolysis, acetic acid and 2,4-pentanedione were added.

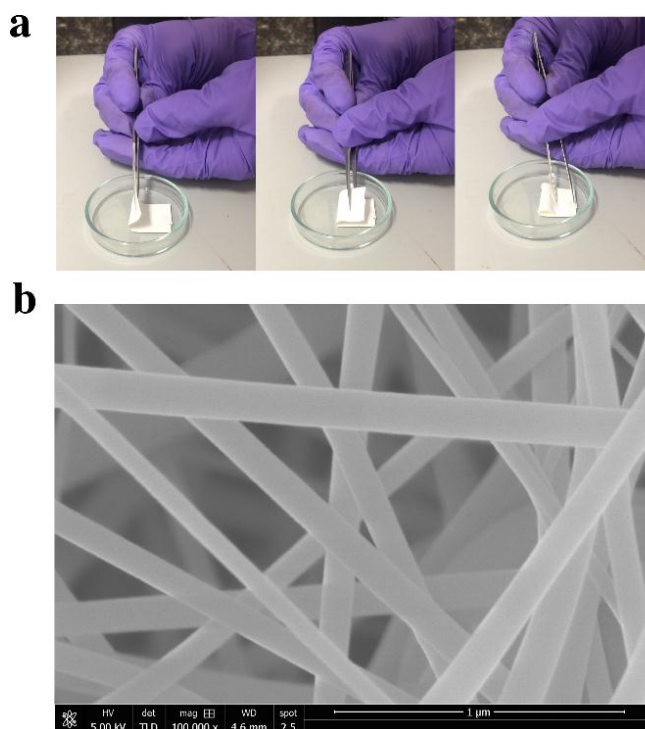


Figure 5.1: (a) Snapshots of TiO₂/PVP Interlayer at Different Bending Angle; (b) SEM Image of TiO₂/PVP Precursor.

In the following electrospinning process, solvents, including ethanol, acid and 2,4-pentanedione were evaporated and a continuous network of TiO₂/PVP was formed due to the rapid hydrolysis in moister air. The obtained TiO₂/PVP precursor was light yellowish and quite flexible, which can be bent even at 180 degrees as shown in **Figure 5.1a**. The microstructure of the precursor was revealed by SEM (**Figure 5.1b**). It can be seen that nanofibers were interconnected and had an average diameter of 120 nm. In addition, each one had a smooth surface, indicating that TiO₂ was uniformly distributed in the PVP matrix.

5.3.2 TiO₂/C Composite

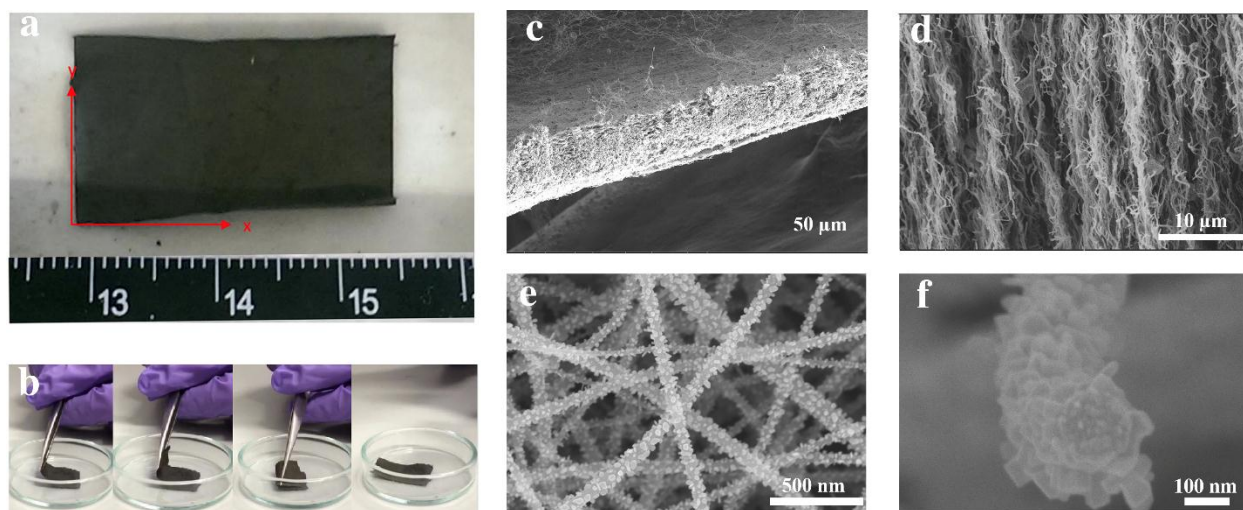


Figure 5.2: (a) Photographs of the As-Prepared TiO₂/C Interlayer; (b) Snapshot of TiO₂/C Interlayer at Different Bending Angle; (c-d) Low and High Magnification Cross-Sectional SEM Images Of TiO₂/C Interlayer; (e, f) Top-View and Cross-Section SEM Images of TiO₂/C Interlayer.

To prepare a TiO₂/C interlayer for lithium sulfur batteries, the TiO₂/PVP precursor was carbonized around 800 °C in N₂ atmosphere. After carbonization, a free-standing black mat was obtained (**Figure 5.2a**), which was as flexible as the precursor (**Figure 5.2b**). To characterize its structure and morphology, scanning electron microscopy (SEM) was carried out. Low and high magnification cross-section SEM images are shown in **Figures 5.2c and 5.2d**, respectively. It can be seen that the hybrid mat had a layered structure with a thickness of 30 μm. The top-view SEM image (**Figure 5.2e**) reveals that the TiO₂/C hybrids possessed a fibrous structure with nanoparticles protruding from the surface, which was quite different from the original PVP-TiO₂ precursor. The average diameter of the nanofiber backbone remained similar before and after carbonization. The newly observed nanoparticles had a polyhedral structure and were uniformly decorated on the surface. The cross-section SEM image of a single TiO₂/C nanofiber (**Figure 5.2f**) confirms that there are small polyhedral particles buried inside the carbon backbone. The size gradient of TiO₂ might be caused by the thermal gradient along the fiber during carbonization. The outer layer of PVP would decompose first and then make a TiO₂ en-riched area, which allow the grain growth of TiO₂. In addition, small TiO₂ deeply buried in side carbon might be driven to the surface because of the small surface energy between nitrogen gas and TiO₂ and be consumed in order to keep the grain growth continuous. The reason for the mat to be so flexible can be attributed to the relatively low volume fraction of TiO₂ within the carbon backbone due to the migration and grain growth of the oxide on the surface.

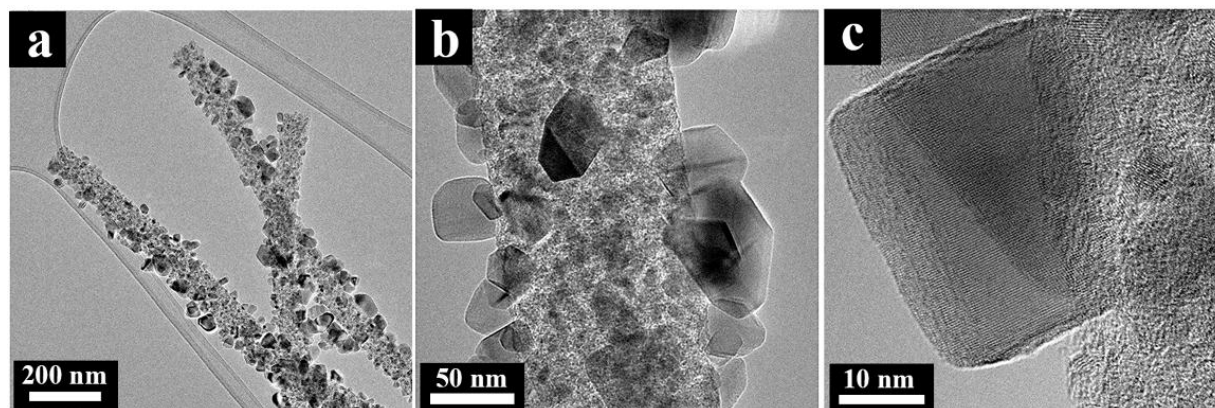


Figure 5.3: (a-c) Low and High Magnification TEM Images of TiO₂/C Nanofibers.

To explore the microstructure of the TiO₂/C hybrids further, transmission electron microscopy (TEM) was performed. From the different magnification TEM images of TiO₂/C hybrids shown in **Figure 5.3a-5.3c**, it can be clearly observed that most nanoparticles decorated on the surface had an average size of 30 nm while smaller nanoparticles (<10 nm) were embedded within. These protruding nanoparticles were TiO₂ grains as determined by the lattice size, which sintered and partially grew out of carbon backbone during high temperature treatment to form a porous core-shell like nano-architecture. More importantly, this structure was very robust and even maintained intact after ultra-sonication, indicating that the small TiO₂ particles trapped inside the fiber could act as a glue. From these TEM images, the pores in the carbon backbone can also be confirmed, which can be filled with electrolyte.

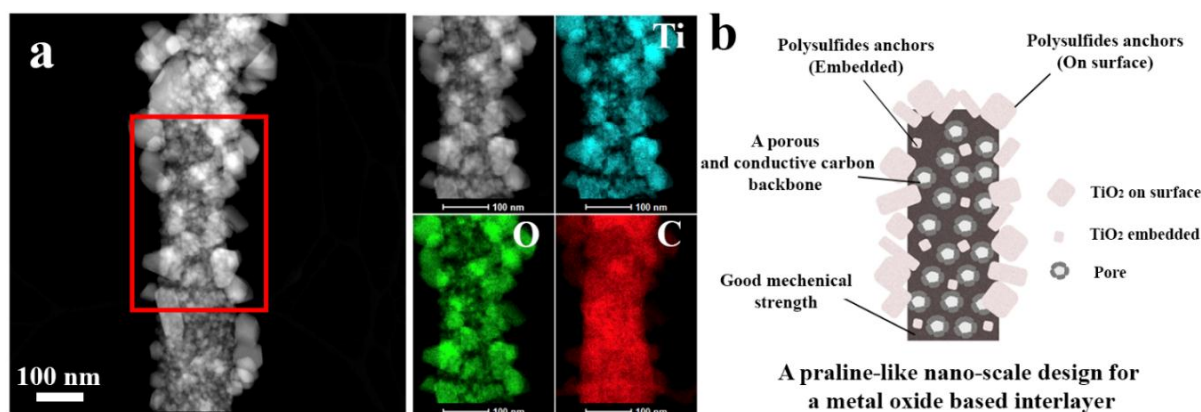


Figure 5.4: STEM Image of a TiO₂/C Nanofiber and Corresponding Elemental Maps.

Figure 5.4a shows the STEM image of a TiO₂/C interlayer with the corresponding elemental mapping of the selected area. It can be seen that carbon was continuously constructed in a fiber like structure while both titanium and oxygen were mainly focused on nano-particles, which had

a distinct size gradient and scattered through the carbon backbone. These results confirms the unique distribution of TiO_2 in the fiber, which was unprecedented in any previous report. The unique praline-like design of this interlayer has the following features (**Figure 5.4b**): (1) High-loading polysulfides anchors; (2) a porous and conductive backbone for fast electron/ion transfer; (3) good mechanical strength and flexibility for structural stability and to accommodate the volume change during reutilization of polysulfides.

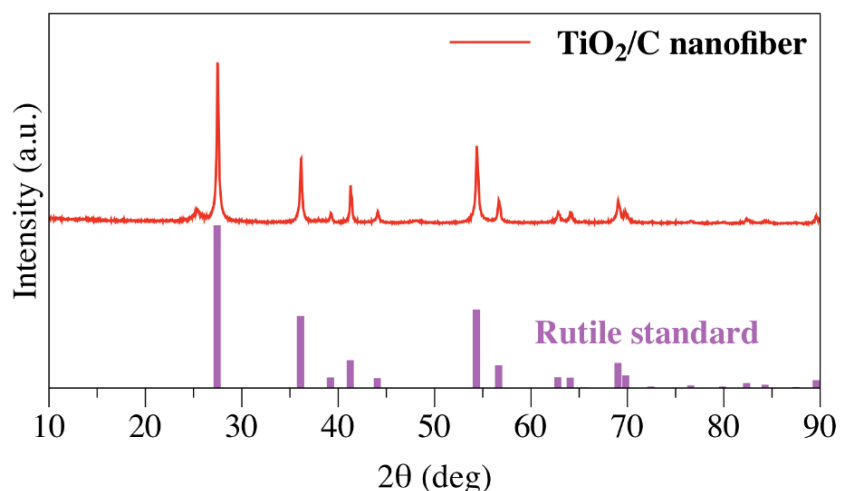


Figure 5.5: XRD Spectrum of TiO_2/C Interlayer.

The phase of the hybrid composite were analysed by XRD. **Figure 5.5** shows the XRD pattern for TiO_2/C composite. Except the broad peak around 26.6, other sharp peaks matched to that of rutile phase with a lattice constant of $a=4.58 \text{ \AA}$ and $c=2.95 \text{ \AA}$. It means the amorphous TiO_2 in the precursor can be completely converted to polycrystalline rutile phase after heat treatment in N_2 atmosphere for 3hr. And the grain size of TiO_2 was determined to be 6.2 nm using Scherrer equation. The broad peak around 26.6 indicates the present of amorphous carbon in the composite, which came from the carbonization of PVP.

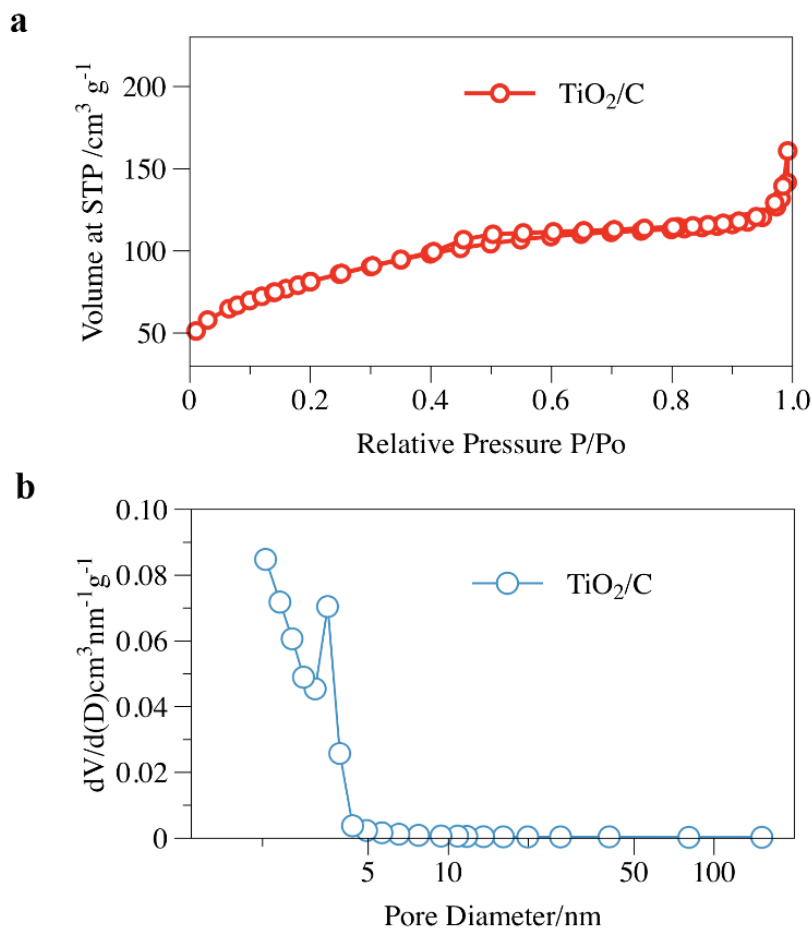


Figure 5.6: (a) Nitrogen Adsorption Isotherms and (b) Pore Size Distribution of TiO₂/C Interlayer.

The texture of the TiO₂/C nanofiber was investigated by N₂ adsorption measurement. The nitrogen adsorption isotherm of TiO₂/C nanofiber is shown in **Figure 5.6** and has a feature of both type I and type IV, indicating TiO₂/C nanofiber had dominant micropores with a limited amount of mesopores. BET results showed that it had a specific surface area of 288.9 m² g⁻¹ and an average pore size of 2.7 nm. The porous structure of carbon backbone mainly contributes to such a high surface area as TiO₂ nano crystals themselves were very dense and only had a specific area of 10 m²/g. The mesopores in the composite could come from the mass transfer of TiO₂ in the fiber while micropores were formed due to the decomposition of PVP.

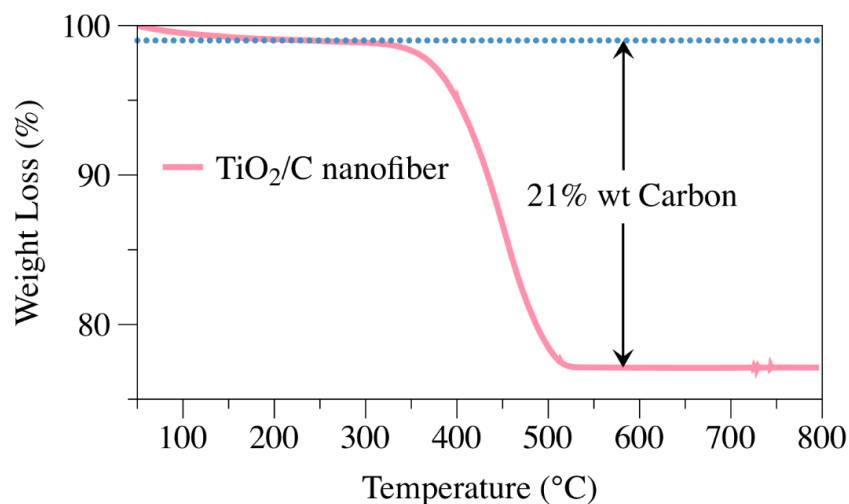


Figure 5.7: TGA Curve of TiO₂/C Interlayer.

To determine the composition of the TiO₂/C, TGA was conducted in air atmosphere at a heating rate of 10°/min. **Figure 5.7** shows the TGA curve of the TiO₂/C composite. At the beginning, there was a small weight loss of 1% due to the evaporation of adsorbed moisture. An obvious weight loss occurred around 400 °C, which can be attributed to the combustion of carbon. Based on the analysis of TGA results, the content of TiO₂ in the composite was around 79 wt%, corresponding to an areal loading of 1.3 mg/cm².

The residual of the sample after the TGA test was further characterized by SEM and XRD. It was found that TiO₂ nanoparticles sintered and grew to form a chain-like structure and carbon was completely removed (**Figure 5.8**). In the XRD spectrum, the previous broad peak around 26 °C disappeared, but no other changes were observed in the TiO₂ peaks, confirming no phase change or decomposition of TiO₂ occurred during the thermal treatment. (**Figure 5.9**).

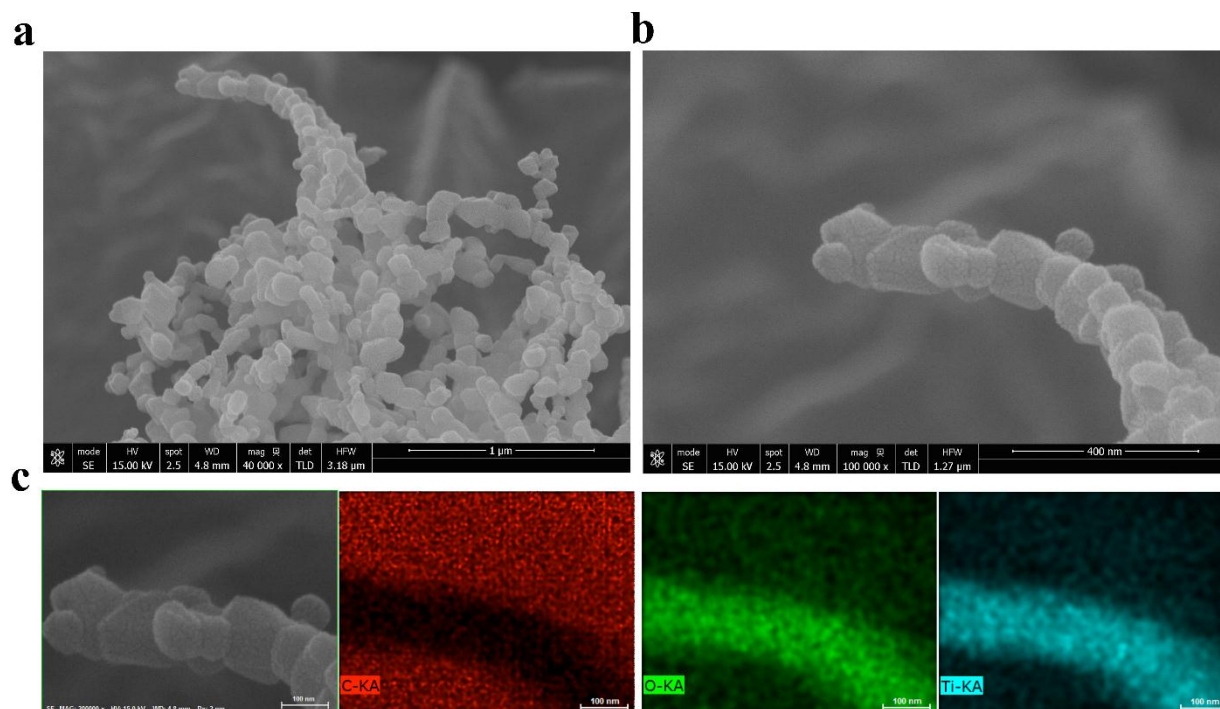


Figure 5.8: (a) Low and (b) High Magnification SEM Images of Samples after TGA; (c) The Corresponding Elemental Maps.

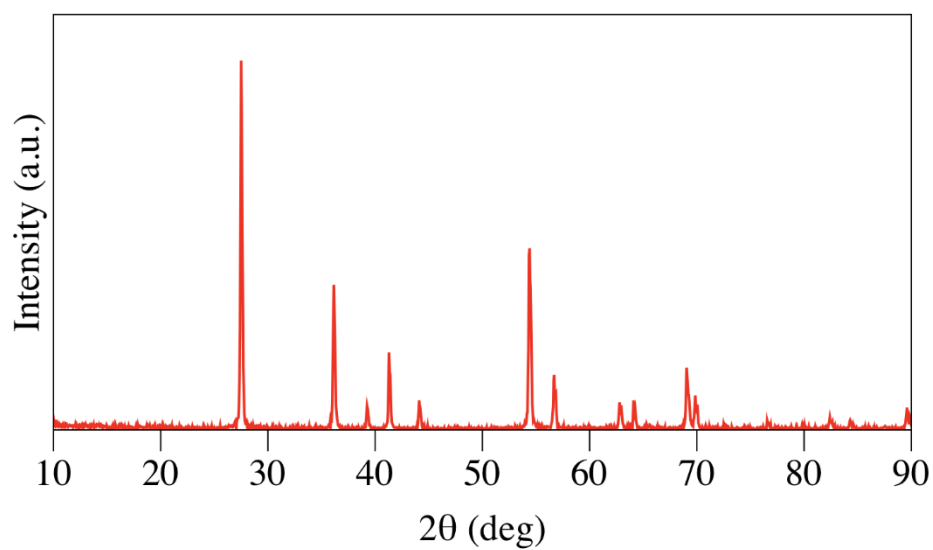


Figure 5.9: XRD Spectrum of Samples after TGA.

5.4 Electrochemical Test and Postmortem Analysis

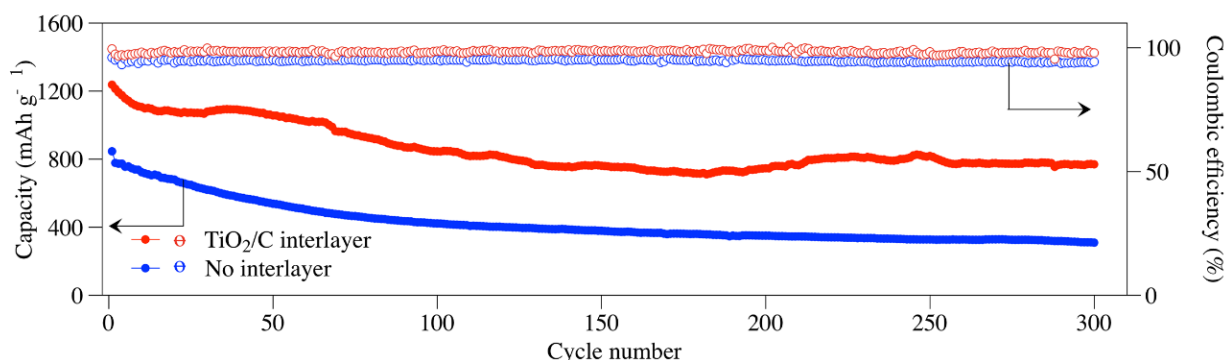


Figure 5.10: Comparison of Cycle-Performance of Sulfur/Carbon Nanotubes Composite Cathode with Different Interlayers at a Current Rate of 0.2C.

In order to investigate how the structure effects the ability to trap and reutilize migrating polysulfides, the hierarchical TiO₂/C interlayer was sandwiched with a S/MWCNT cathode, whose electrochemical performance was tested using Li as an anode. A good capacity and cycle life are achieved after deep cycling as shown in **Figure 5.10**. With the incorporation of the hybrid TiO₂/C interlayer, the initial discharge capacity of the S/MWCNT cathode increased from 847.8 to 1238 mAh g⁻¹, about 74% of the theoretical value (1675 mAh g⁻¹) calculated on the basis of the mass of active sulfur. An incremental phenomenon of discharge capacity after 30 cycles was observed, which can be attributed to the gradual infiltration of electrolyte through TiO₂/C interlayer and into S cathode. After 300 discharge/charge cycles, it maintained a reversible capacity of 770.8 mAh g⁻¹ with a capacity retention of 62%, which is about 25% higher than the one without flexible interlayer. In addition, there was a 5% increase in the average Coulombic efficiency for the S/MWCNT cathode with a TiO₂/C interlayer, obtaining at ~99%.

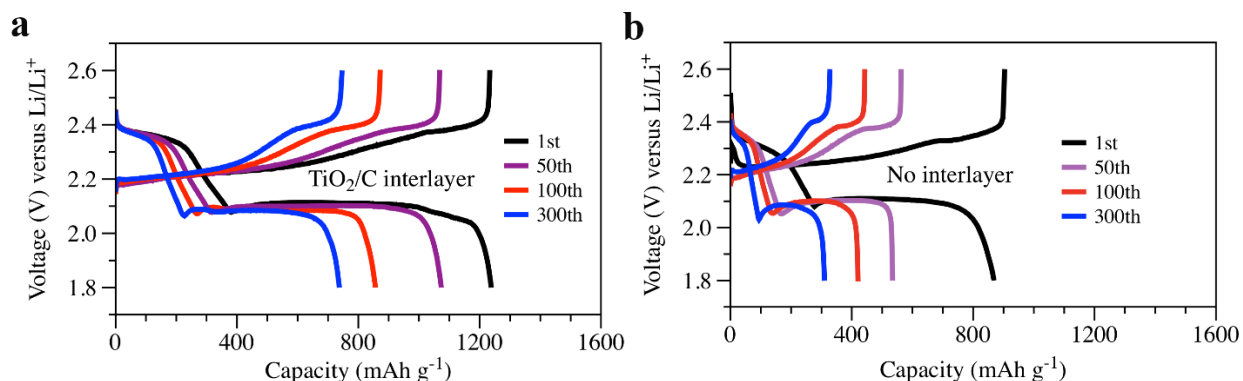


Figure 5.11: Discharge-Charge Profiles of S/MWCNT Composite with (a) TiO₂/C Interlayer and (b) No Interlayer.

Figure 5.11a and 5.11b show the galvanostatic discharge/charge profiles of S/MWCNT cathode with and without interlayer in the 1st, 50th, 100th and 300th cycle, respectively. All exhibit a typical two-plateau behavior during discharge, corresponding to the multi-step reaction mechanism of sulfur involved. Specifically, the high plateau at 2.3V is attributed to the formation of long-chain polysulfides (Li_2S_n , $4 \leq n < 8$) from the open ring of cyclo-S₈ while the low plateau at 2.1V is assigned to the reduction of long-chain polysulfides to short-chain polysulfides (Li_2S_n , $n < 4$) and even all the way to lithium sulfide (Li_2S). Based on the analysis of variation of profiles in different cycles, it is also confirmed that the TiO₂/C interlayer provides better cycle stability of the S/MWCNT cathode. For S/MWCNT cathode without interlayer, its second plateau decreased rapidly during the first 50 cycles, whereas, that of the cathode with interlayer reduced much slower and an obvious decay happened during the second 50 cycles, which could be attributed to the saturation of sulfur species adsorbed on the interlayer.

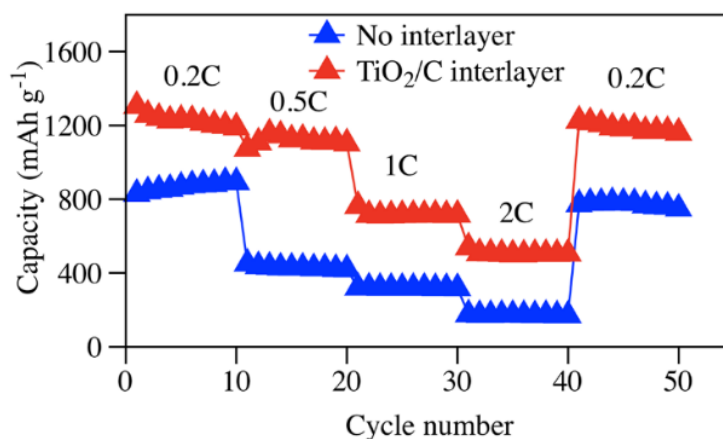


Figure 5.12: Rate-Performance of S/MWCNT Composite with (a) TiO₂/C Interlayer and (b) No Interlayer.

Figure 5.12 compares the rate performance of S/MWCNT cathodes with different interlayers at a step-wise current rate from 0.2 to 2C and back to 0.2C. After the first 10 cycles at 0.2C, the capacity of S/MWCNT cathodes with TiO₂/C interlayer was maintained at 1188.8 mAh g⁻¹, which gradually reduced to 1102.3 mAh g⁻¹ and eventually to 715.4 mAh g⁻¹ at the end of each tenth-cycle test at 0.5C and 1C, respectively. Remarkably, this structure even delivered an average capacity of 504.8 mAh g⁻¹ at 2C and recovered to a reversible capacity of 1160.7 mAh g⁻¹ when the current rate returned to 0.2C. In contrast, cathode with no interlayer exhibited much lower performance. It delivered a reversible capacity of 892.1 mAh g⁻¹ at the end of the first 10 cycles at 0.2C and had a dramatic capacity drop to 450.7 mAh g⁻¹ when the current rate increased from 0.2C to 0.5C. At the end of each tenth-cycle at 0.5C and 1C, it had a reversible capacity of 419.3 and 320.2 mAh g⁻¹, respectively. When the current returned to 0.2C, a reversible capacity of 760.2 mAh g⁻¹ was obtained.

Figure 5.13a and 5.13b show the typical discharge-charge profiles of the S/MWCNT cathode with different interlayers at current rates ranging from 0.2 C to 2C. The cathode incorporating the TiO₂/C interlayer exhibited much better rate tolerance, with little change in plateau potential at differing rates. Even at 2C, the second plateau still maintained at a potential around 2V. However, the one for cathode with no interlayer dropped to a potential below 1.9V. The superior rate performance of the S/MWCNT cathode with the hybrid interlayer compared to that of controlled experiments is attributed to its relatively low charge transfer resistance (R_{ct}) as evidenced by electrochemical impedance spectroscopy (EIS) (**Figure 5.14**). Both plots were in the form of a semi-circle at high frequency region and a short line in the low-frequency region. The diameter of semi-circle at high frequency is related to the R_{ct} . After the incorporation of TiO₂/C interlayer, the R_{ct} is reduced from 135 to 40 Ω , indicating that the interlayer can act as an upper current collector to reduce the interfacial resistance between cathode and electrolyte.

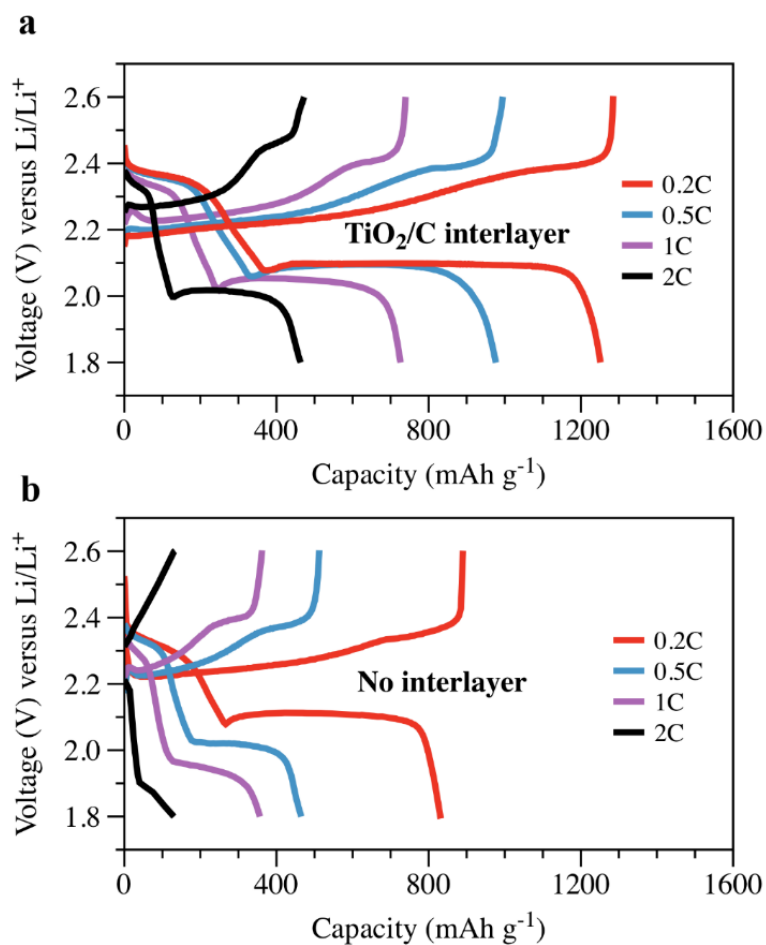


Figure 5.13: (a) Rate Performance Discharge-Charge Curves of the S/MWNCT Cathode with TiO_2/C Interlayer at Different Current Rates; (b) Discharge-Charge Curves of the S/MWNCT Cathode with No Interlayer at Different Current Rates.

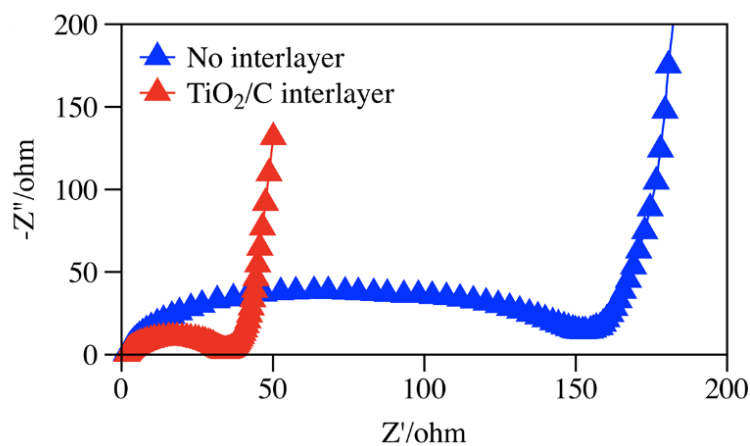


Figure 5.14: Nyquist Plots of AC Impedance Spectra of S/MWNCT Cathode with Different Interlayers.

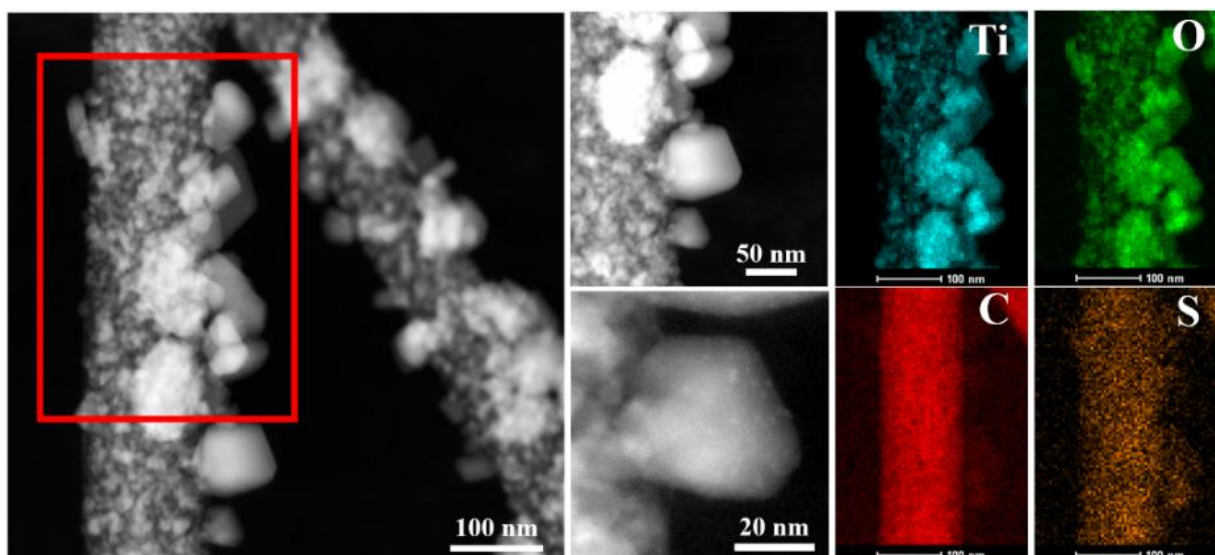


Figure 5.15: STEM Images of Cycled TiO_2/C Interlayer with Corresponding Elemental Maps.

After 300 deep cycles at 0.2C, the TiO_2/C interlayer was recovered and its morphology was analyzed by STEM. As shown in **Figure 5.15**, the praline-like nano-architecture survived intact, which is one reason for the effective trapping of polysulfide during long cycles. From the magnified STEM images, small nano dots were observed on the TiO_2 nanoparticles protruding from the surface, which might be adsorbed sulfur species. The mapping of the selected area confirms the uniform distribution of S in the whole nano-architecture.

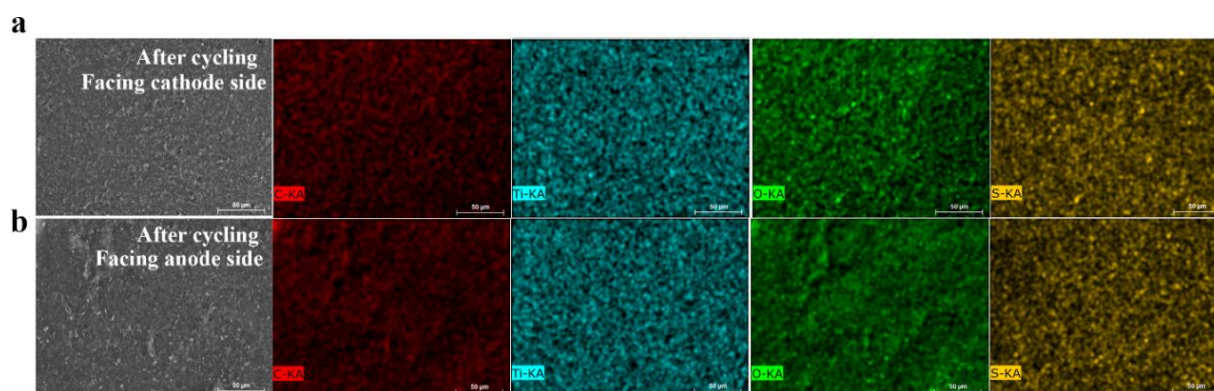


Figure 5.16: SEM Images of the Fresh Cycled TiO_2/C Interlayer with Corresponding Elemental Maps: (a) Facing Cathode Side; (b) Facing Anode Side.

Large area EDS mapping was also conducted on both sides of the cycled interlayer (**Figure 5.16a and 5.16b**). After cycling, the surface of the hybrid interlayer became rough due to the trap of polysulfides species. S signal was detected on both sides of the cycled interlayer, but was more intense on the side facing cathode, confirming the role of the hybrid interlayer in confining polysulfides.

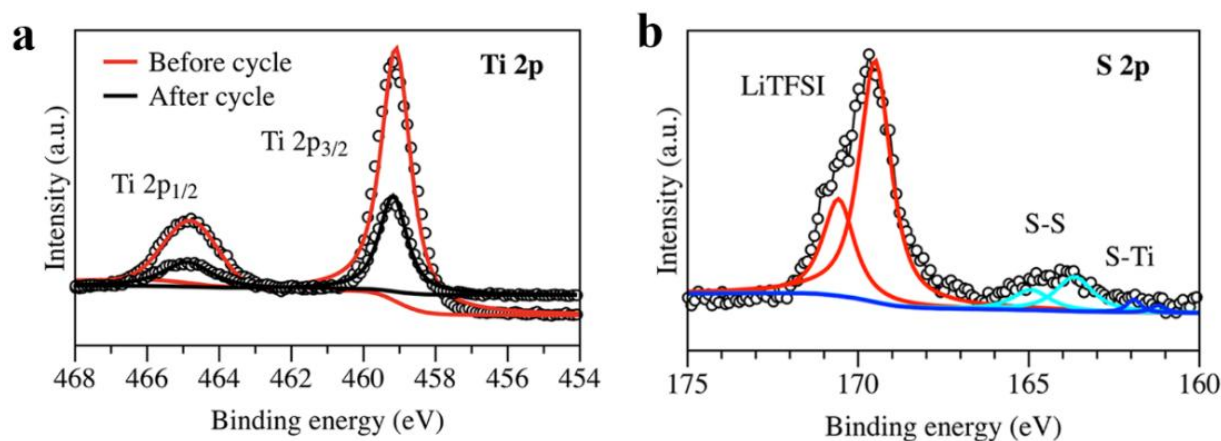


Figure 5.17: (a) Comparison of Ti_{2p} XPS Spectrum of the Hybrid Interlayer before and after Cycling; (b) S_{2p} XPS Spectrum of the Cycled Interlayer.

To investigate the chemical composition of cycled TiO₂/C interlayer, XPS was conducted. **Figure 5.17a and 5.17b** show the Ti_{2p} and S_{2p} XPS spectra of the cycled interlayer, respectively. Characteristic peaks of Ti_{2p} are observed at 459.1 eV and 464.8 eV slightly shifted to a higher energy (by 0.2 eV) after cycling, which is attributed to the chemical interaction between the TiO₂ and S species. In addition, the peaks at around 162.1 eV and 161.2 eV in the spectrum of S_{2p} confirm the Ti-S binding. These results further evidence the chemical effects of TiO₂ on molecular confinement of polysulfides.

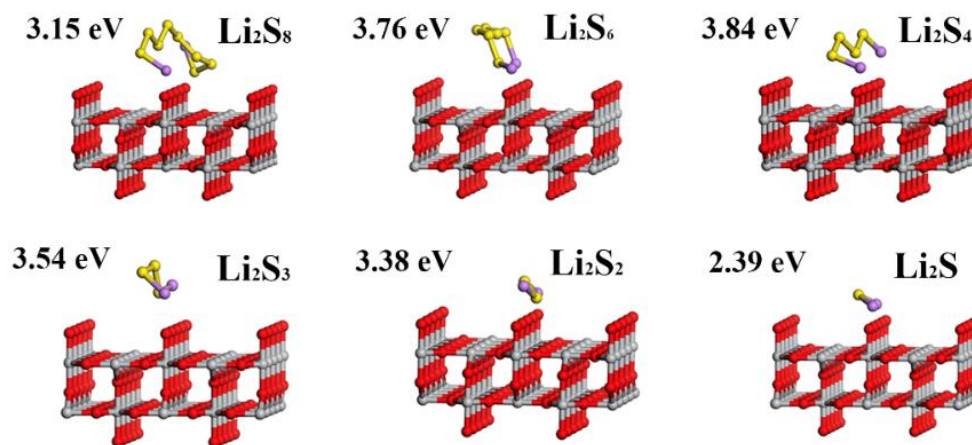


Figure 5.18: Configurations for the Binding of Five S Species on Rutile-TiO₂ (110) Surface.

To better understand the chemical effects of TiO₂ on molecular confinement of polysulfides, the binding energies of the TiO₂ and five relevant S species were obtained by DFT calculations, which ranged from 2.39 eV to 3.84 eV as shown in **Figure 5.18**. TiO₂ exhibited a much stronger chemical affinity to polysulfides with different molecular lengths than carbon, indicating the bonding mainly originates from Li-O bonds.

5.5 The Derivatives of TiO₂/C Composite

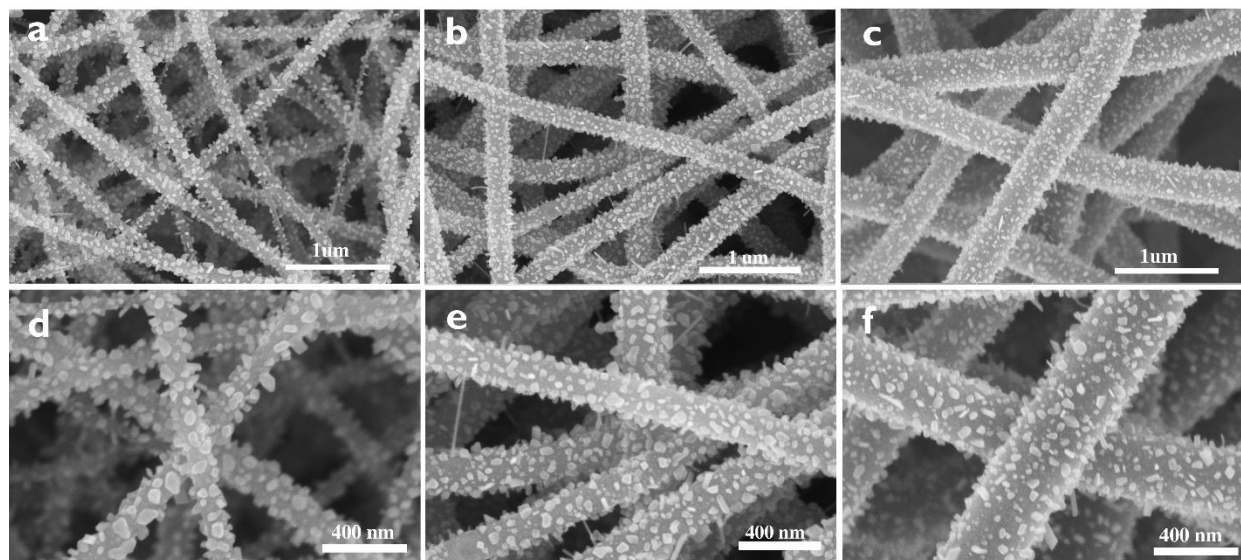


Figure 5.19: SEM Images of Electrospun TiO₂/C Nanofibers Using Different PVP Concentration: (a, d) 0.03 g ml⁻¹; (b, e) 0.05 g ml⁻¹; (c, f) 0.07 g ml⁻¹.

PVP content in the precursor was further increased from the original 0.03 to 0.07 mg L⁻¹ and the corresponding carbonized samples were indexed as 003TiO₂, 005TiO₂, 007TiO₂, respectively. The effects of PVP concentration on the morphology of the carbonized TiO₂/C nanofibers was investigated by SEM. As shown in **Figure 5.19**, all TiO₂/C hybrids exhibited fibrous structure with nanoparticles protruding from the surface. With increasing PVP concentration in the precursor, the average diameter of nanofibers was increased from 120 to 400 nm, whereas the size of protruded nanoparticles was decreased from 50 to 10 nm. It implies carbon could inhibit the sinter and growth of TiO₂ nano crystals during the heat treatment. Interestingly, among the three samples, only 003TiO₂ with a large amount of TiO₂ nano crystals decorating on surface kept flexible, indicating the mole ratio of TiO₂ to carbon in the backbone is an important factor that determines the flexible nature of the composite. The more the TiO₂ nano particles grow out, the smaller the mole ratio is. However, if most TiO₂ nanoparticles come out, the hierarchical structure may not be stable due to the stress on surface. It is, therefore, postulated that the value of this mole ratio should lie in a suitable range.

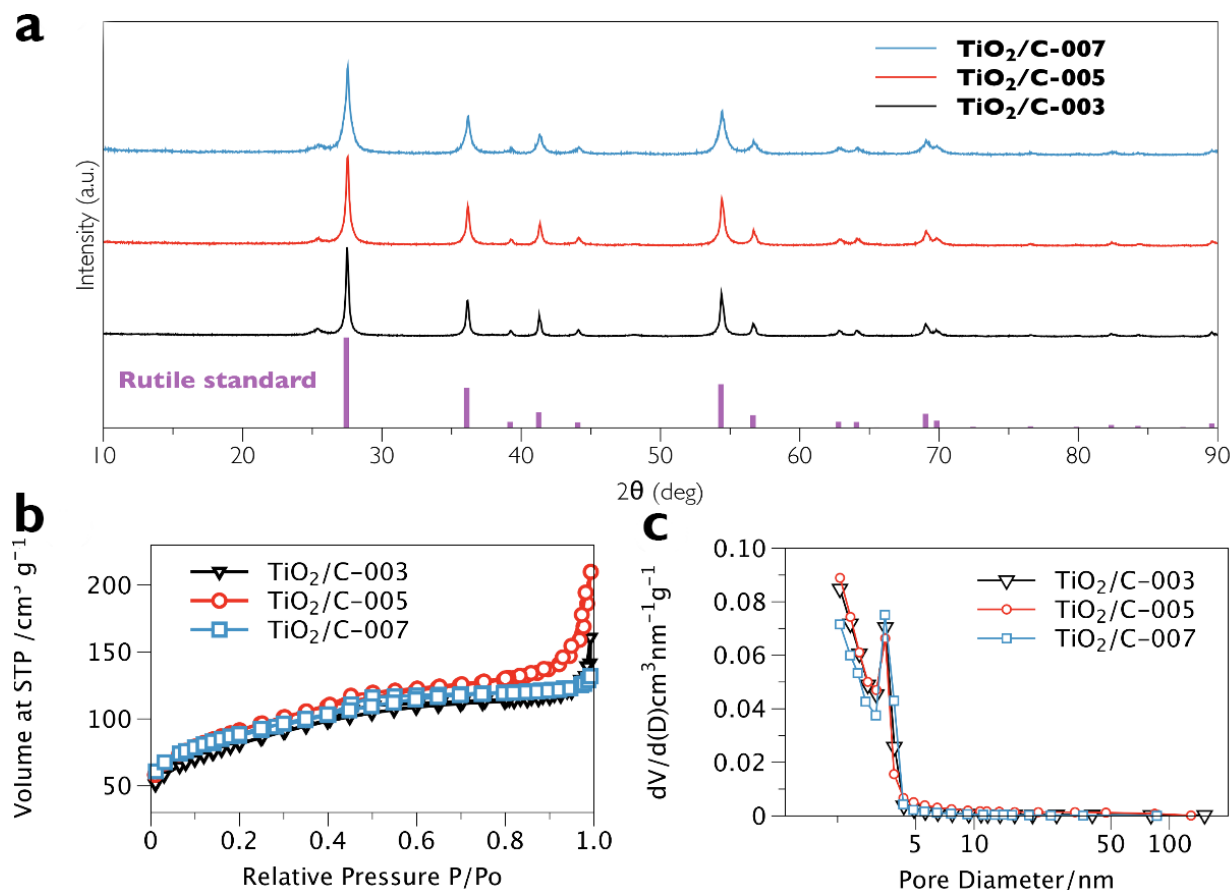


Figure 5.20: Electrospun TiO_2/C Nanofibers Using Different PVP Concentration: (a) XRD Patterns; (b) Nitrogen Sorption Isotherms and (c) Pore Size Distribution Calculated from the Desorption Branch.

As shown in **Figure 5.20a**, the XRD patterns for electro-spun TiO_2/C nanofibers using different PVP concentration were similar and matched to that for rutile phase. These results indicate that the phase of TiO_2 in the composite only depends on the carbonization temperature. However, TiO_2 003 sample had the smallest full widths at half maximum of the characteristic peak around 27° , corresponding to the largest grain size, which was consistent with the previous SEM results.

In addition, all samples had a similar BET surface area of $300 \text{ m}^2 \text{g}^{-1}$ and an average pore size of 3 nm (**Figure 5.20a and 5.20b**). It means the BET surface area of TiO_2/C composite is a balance of diameter of fiber and carbon content. 003 TiO_2 sample had the smallest diameter, but the least amount of carbon content. As a result, the contribution to specific area from smaller diameter was compensated by its lower carbon content. In terms of the pore size distribution, it might come from the intrinsic properties of PVP and depend on one of the carbonization parameters—temperature.

The effect of temperature on the evolution of morphology and composition of the 005TiO₂/PVP precursor was also investigated. Compared to two other samples, 005TiO₂/PVP sample had a suitable content of carbon and thus the growth of TiO₂ nano crystals during heat treatment was moderately controlled. The sample was carbonized at three different temperature ranging from 800 to 1000 °C.

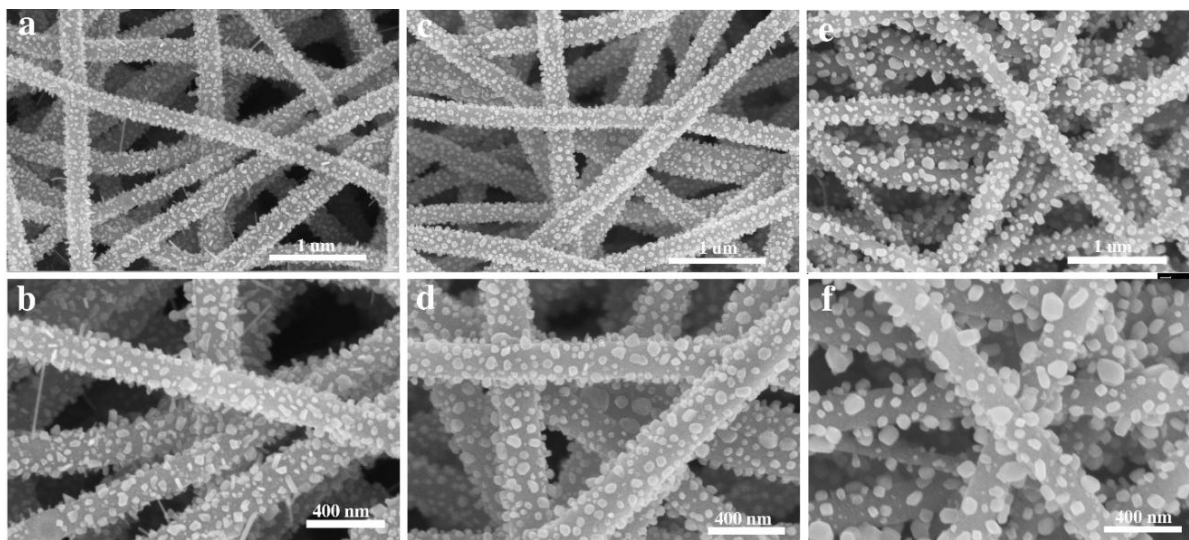


Figure 5.21: Low and High Magnification SEM Images of TiO₂/PVP Precursor after Carbonization at Different Temperature: (a, b) 800 °C; (c, d) 900 °C, (e, f) 1000 °C.

The SEM images of sample after carbonization at different temperature are shown in **Figure 5.21**. Temperature had a direct effect on the size and density of nanoparticles decorated on the surface. With increasing temperature, the particle size was increased from approximately 30 nm to 150 nm while the diameter of the carbon backbone remained almost the same around 200 nm, indicating temperature is a main driving force for the grain growth. Another interesting discovery is that the density of the particles on the surface dramatically reduced when the temperature reached 1000 °C. One hypothesis to explain this phenomenon is that the small nanoparticles on the surface tend to agglomerate in order to minimize the surface energy. As the particle size increased, the gap between individual particles gradually became smaller, finally leading to the contact and agglomeration of particles.

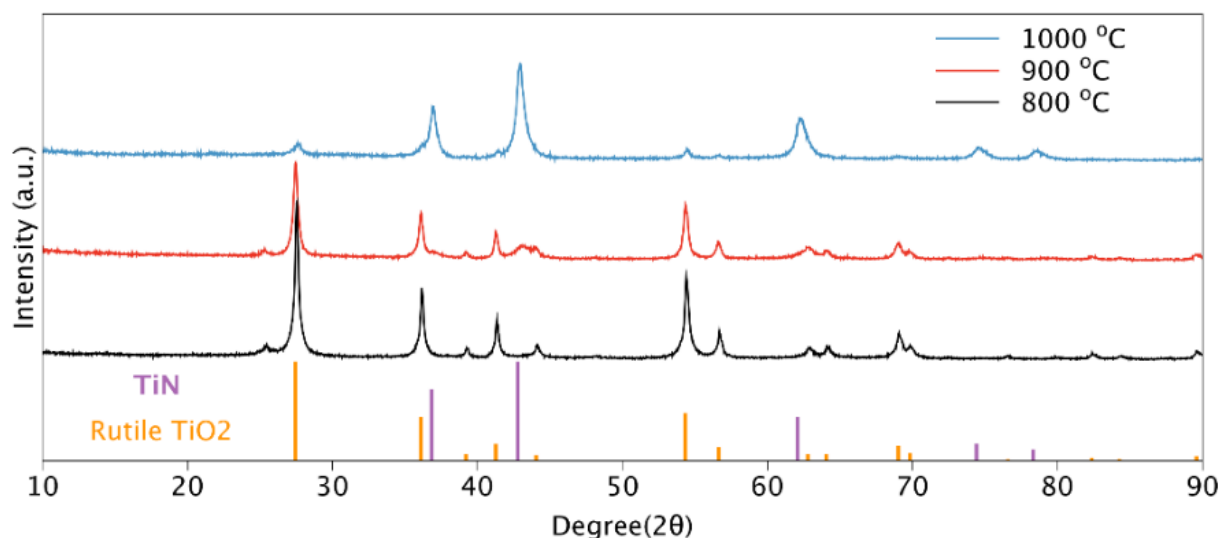


Figure 5.22: XRD Patterns for the TiO₂/PVP Precursor after Carbonization at Different Temperature.

Temperature also affects the phase of the TiO₂/PVP precursor after carbonization. The XRD patterns for the TiO₂/PVP precursor after carbonization at different temperature are shown in **Figure 5.22**. At 800 °C, only rutile phase of TiO₂ was identified in the sample, but a new phase was observed when the temperature reached 900 °C, which could be attributed to the formation of titanium oxynitride arising from the reduction of TiO₂ with carbon in the presence of N₂. When the temperature was further increased to 1000°, the characteristic peak of TiO₂ around $2\theta = 27^\circ$ was remarkably reduced while new sharp peaks around $2\theta = 37^\circ$ and 43° appeared, indicating that rutile phase TiO₂ was gradually transferred to TiO_{1-x}N_x with a cubic rock-salt structure. The average crystallite size of the TiO_{1-x}N_x particle was 20 nm, calculated using Scherrer equation.

Although the morphology and phase of the samples changed a lot as the temperature increased, their BET surface area and average pore size still maintained almost the same. As shown in **Figure 5.23**, all samples had a similar specific surface area around 330 m²/g and an average pore size of 3 nm. These results confirmed that the specific surface area mainly depends on the intrinsic property of PVP itself instead of the carbonization temperature.

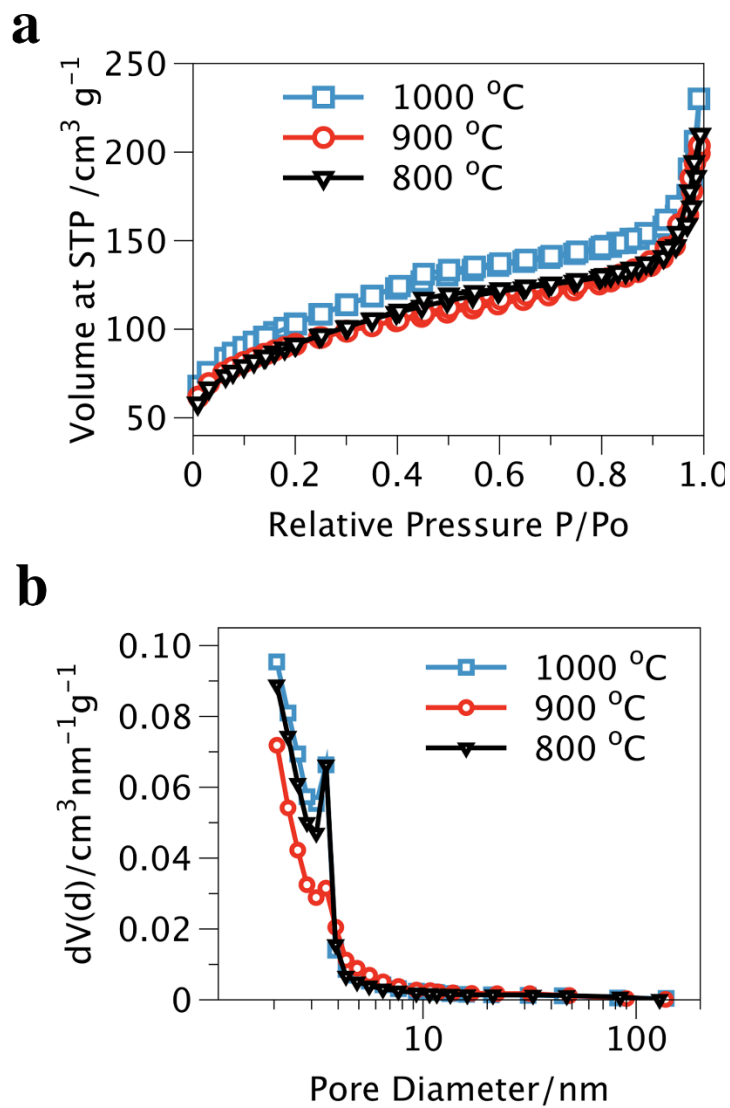


Figure 5.23: (a) Nitrogen Sorption Isotherms and (b) Pore Size Distribution Calculated from the Desorption Branch.

5.6 Summary of this Chapter

In conclusion, an enhancement in cycle stability and rate capability of a S/MWCNT composite cathode has been achieved by incorporating a praline-like flexible interlayer consisting of TiO_2 nano particles and carbon fibers. The chemical effect of TiO_2 on capturing and confining polysulfides takes place throughout the nano-architecture. Meanwhile, the conductive carbon nanofiber backbone supplies an inter-connected network for fast electron and ion transfer. More importantly, this system offers enough mechanical strength to support a high number of TiO_2 nanoparticles to maximize their chemical role and to accommodate the volume change arising from the re-utilization of polysulfides. The design of chemi-functional interlayers by in-situ integration of metal-oxide nanoparticles with carbon fibers is a promising approach toward optimizing the polysulfide capture and reutilization process, with the potential to advance the chemistry of lithium-sulfur batteries for practical applications in the future.

In terms of the formation mechanism of praline-like TiO_2/C nanofiber itself, it was found that temperature is a driving force for the growth of TiO_2 grains and has a direct effect on the phase of the sample. Pure rutile phase TiO_2 was obtained around 800°C , which was gradually transferred to cubic phase titanium oxynitride as temperature reached 1000°C . As the nano particles kept growing, they may contact each other and agglomerate on the surface to form a praline-like structure. On the other hand, carbon served as a scaffold for TiO_2 and prevent TiO_2 from growing. Initially, the surface of the scaffold might decompose due to thermal gradient to form a TiO_2 -enriched area, which triggered the grain growth. In addition, the specific surface area of samples was also mainly determined by carbon. All samples had a similar specific surface area when the carbonization temperature was in the range of $800\text{-}1000^\circ\text{C}$. More importantly, the flexibility of the sample might depend on how much TiO_2 is left in the carbon after the heat treatment.

Chapter 6 A Dual-Interlayer Consisting of Carbon and Titanium Nitride for an Oval-Like Carbon/Sulfur Cathode

6.1 Overview of the Work

Carbon interlayers have been proved to be useful in order to improve the capacity of sulfur cathodes, but they are not efficient enough to mitigate the capacity decay during cycling because of the weak interaction between non-polar carbon and polar polysulfides. In the previous two chapters, two kinds of metal-oxides (ZnO and TiO_2) have been integrated with an electro-spun carbon nanofiber mat via an ex-situ and in-situ route respectively in order to enhance the confinement of polysulfides with a strong chemical bond between oxygen in metal oxides and lithium in lithium polysulfides (Li-O bond). Because of the poor conductivity of metal oxides, it necessitate the intimate contact of nano-structured metal oxides with the carbon framework to ensure fast electron transfer. Therefore, a well-defined hierarchical structure (like brush or praline) is required for metal oxide based interlayer.

In this chapter, a new concept of dual interlayer was proposed. It gives a much easier way to modify the non-polar carbon interlayer by simply coating conductive polar nanoparticles on surface. To give a proof of concept, commercially-available titanium nitride (TiN) nanoparticles was coated on the as-prepared electro-spun carbon nanofiber. The fabrication of this dual interlayer is quite facile, would leading to a low cost industry manufacturing. The distinct two-layered microstructure of the interlayer was characterized by SEM, XRD and Raman. To investigate its effect on the electrochemical performance, the TiN/C interlayer was coupled with an oval-like carbon/sulfur composite cathode, which had a sulfur loading approximately 3 times that of the previously used sulfur/carbon multi-walled nanotube composite cathode. The chemical role of TiN in adsorbing polysulfides was investigated by the characterization of the morphology and composition of the cycled interlayer as well as the calculation of binding energy using DFT theory.

6.2 The Methods

6.2.1 Synthesis of an Oval-Like Carbon/Sulfur Composite Cathode

An oval-like carbon was received from Beijing Institute of Technology and was directly used as a conductive matrix. Sulfur (S) was incorporated in the oval-like carbon (OLC) using a wet chemistry method. Briefly, 100 mg OLC was first mixed with 0.025M sodium thiosulfate solution under intense stirring for 30 min. Then, 1M hydrochloric acid solution was added dropwise to the solution, which was under both ultrasonic and mechanical agitation for 4h. The as-prepared OLC/S composite was mixed with carbon black and LA132 binder in a mass ratio of 80:12:8 in NMP solvent. The slurry was then cast on the aluminum foil, followed by drying in an oven at 60 °C for 24 h. The electrodes were cut into discs that had a diameter of 11 mm and a sulfur loading of 8.5 mg cm⁻².

6.2.2 Fabrication of TiN based Dual-Interlayers

Commercially-available titanium nitride nanoparticles powder was mixed with PVDF binder in a ratio of 1:1 in NMP solvent. The slurry was then coated on the surface of the previously prepared electro-spun carbon nanofibers mat using doctor blade. The wet interlayer was put in an oven at 60 °C for 12 hours to evaporate NMP solvent.

6.3 Microstructure and Morphology Characterization

6.3.1 A Oval-Like Carbon/Sulfur Composite Cathode

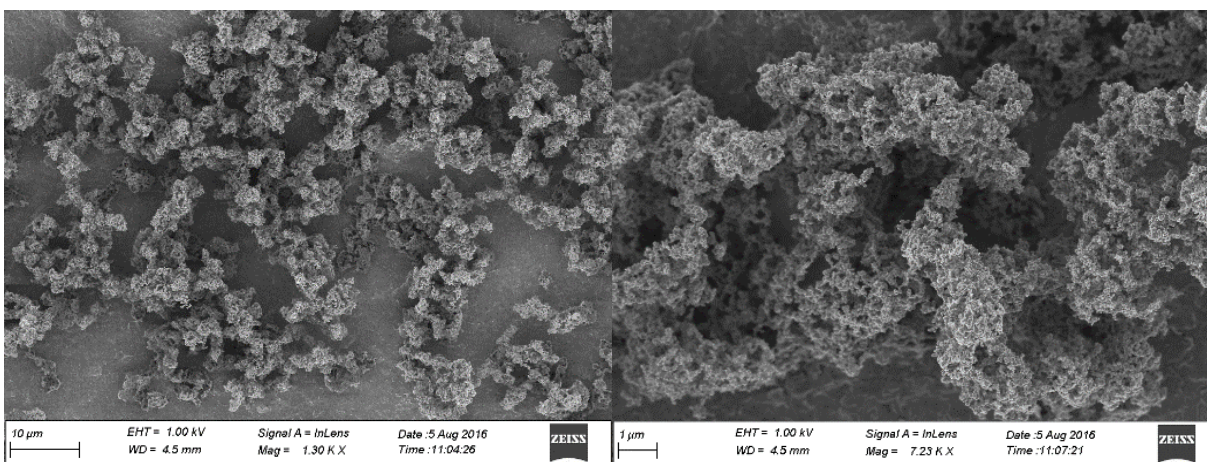


Figure 6.1: Low and High Magnification SEM Images of the Assembled KB.

The received carbon was assembled Ketjen black (KB), which is one of the promising carbon materials for electrochemical tests due to its good conductivity and large specific surface area. **Figure 6.1** shows the low and high magnification SEM images of the assembled KB. It can be seen that KB nanoparticles were assembled into granules with an oval-like microstructure. Each granule consisted of thousands of KB nanoparticles and had a diameter of approximately 2 μm . The assembly of KB was achieved by molecular links. According to previous study^[187], the surface modification of KB was initially done by concentrated nitric acid treatment. Nitric acid is a strong oxidant and can react with KB to introduce carboxyl groups on surface ($-\text{COOH}$). The assembly of these modified KB was further realized via a double “Fischer esterification” with the help of phytic acid and ethylene glycol. Polyphosphate ester was formed between phosphoric acid group and ethylene glycol while polycarbonate ester was generated between carboxyl group and ethylene glycol. Both esters can serve as molecular links to glue the scatter KB nanoparticles together. More importantly, carbonizing esters can make these links conductive. To make a thick sulfur electrode for practical application of Li-S batteries, it is necessary to link these KB nanoparticles to form a microstructure, which could offer high tap density and sulfur loading. In addition, the surface modification of KB should enhance the intimate contact between current collector (Al foil) and cathode materials and thus prevent the thick cathode from cracking during the slurry drying process.

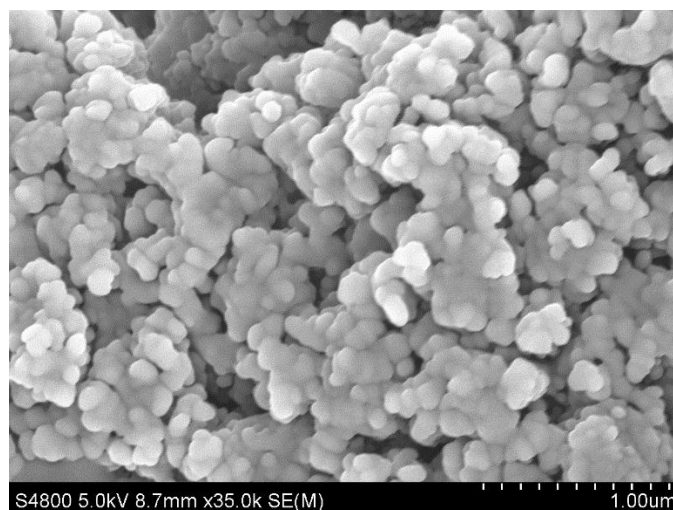


Figure 6.2: SEM Image Assembled KB/S Composite.

A key feature of this assembled KB is its structural stability. The packed KB nanoparticles offered stable inter-particle contact and provided fast electron transfer path. In addition, the space inside the structure can not only hold electrolyte, but also accommodate volume change of sulfur species during charging and discharging. Because of the above benefits, the assembled KB nanoparticles were used as a conductive host for sulfur, which heterogeneously nucleated as thiosulfate ion reacted with HCl in a KB dispersed solution. **Figure 6.2** shows the SEM image of the assembled KB/S composite. After sulfur impregnation, the surface of the KB nanoparticles became darker and smoother, implying that most of the pores of the KB nanoparticles were fully filled with sulfur and part of the sulfur was also coated on the surface. KB still maintained a sphere-like morphology, but its diameter increased from 70 to 100 nm.

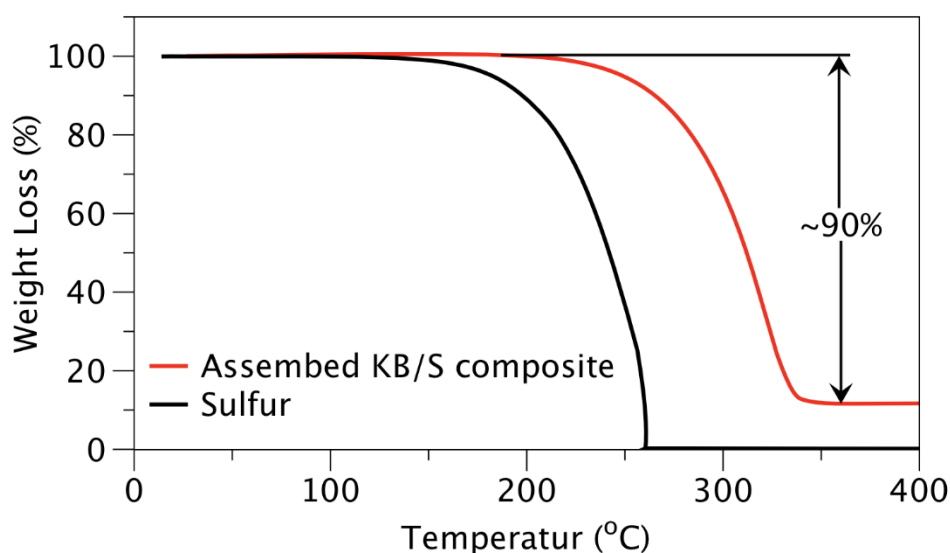


Figure 6.3: TGA Curves of Assembled KB/S Composite and Sulfur.

To determine the sulfur content of the composite, TGA was conducted in air atmosphere at a heating rate of 10 °C. **Figure 6.3** shows the TGA curves of the assembled KB/S composite and sulfur, respectively. Both curves had one main weight loss due to the combustion of sulfur in the air. However, the weight loss for assembled KB/S composite occurred at around 60 °C higher than that for sulfur itself, indicating the strong chemical binding between carbon and the precipitated sulfur. Based on the TGA analysis, the sulfur content of the composite was approximated 90 wt%.

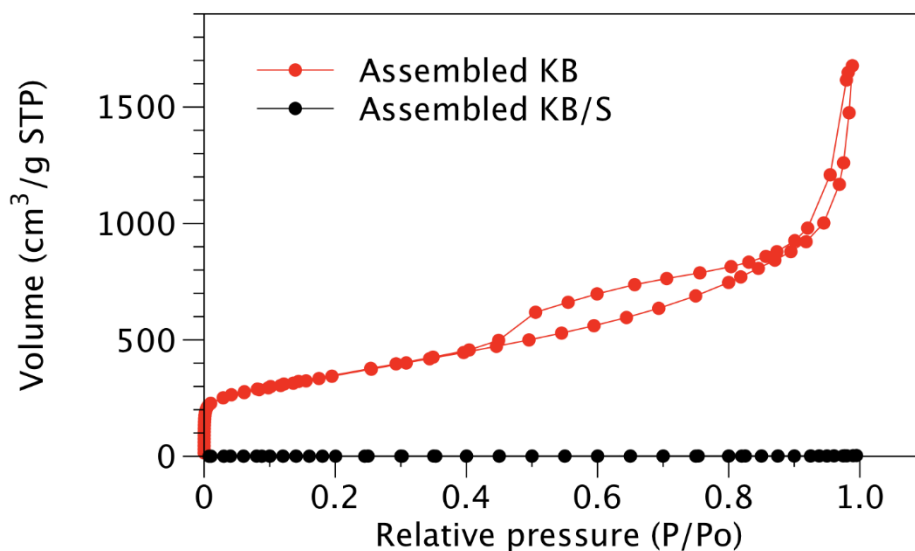


Figure 6.4: N₂ Adsorption/Desorption Isotherm Curves of Assembled KB and Assembled KB/S Composite.

Sulfur was heavily loaded in the assembled KB particles in a uniform way. To find the reason, N₂ sorption measurements were conducted to investigate the specific surface area of assembled KB nanoparticles and assembled KB/S composite. As shown in **Figure 6.4**, the N₂ adsorption/desorption isotherm curve of assembled KB is IV type with a hysteresis loop, indicating its mesoporous structure. The assembled KB had a specific surface area of ~1209 m² g⁻¹ and pore volume of 2.55 cm³ g⁻¹, which not only offered enough room for loading sulfur, but also enabled fast sulfur nucleation and a uniform precipitation of small sulfur particles. After sulfur was precipitated, the specific surface area and pore volume of assembled KB dramatically reduced to about 1.3 m² g⁻¹ and 0.005 cm³ g⁻¹, respectively, suggesting the pores of the assembled KB were completely filled up when the sulfur loading is around 90%.

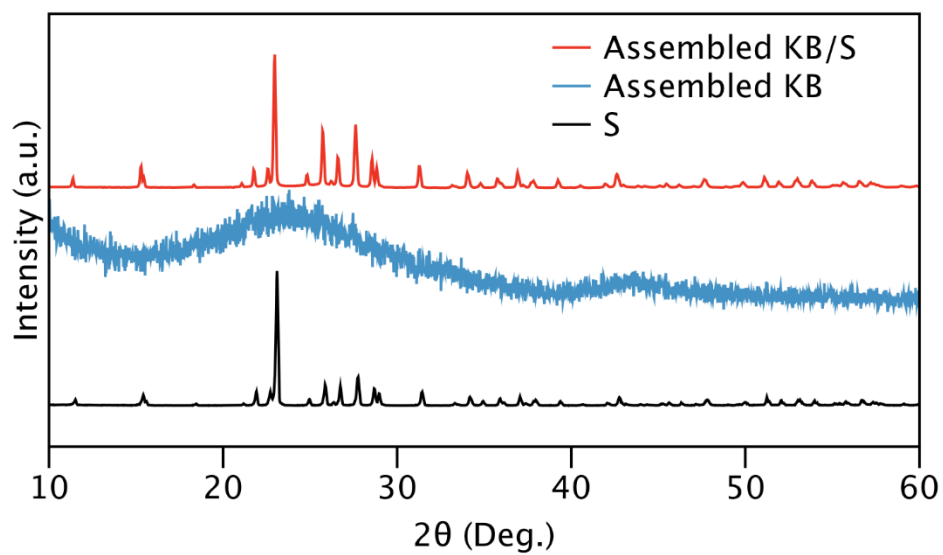


Figure 6.5: XRD Patterns of Sulfur, Assembled KB and Assembled KB/S Composite.

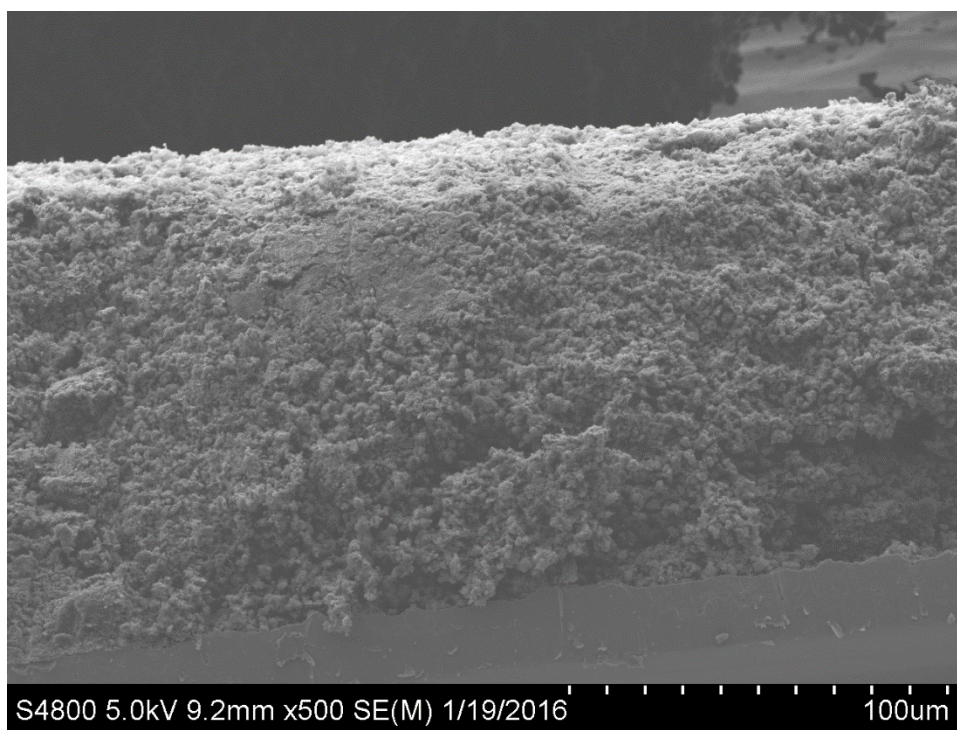


Figure 6.6: Cross-Section SEM Image of Assembled KB/Sulfur Composite Cathode.

The phase of the assembled KB/sulfur composite were investigated by XRD. **Figure 6.5** shows the XRD spectra for sulfur, assembled KB and assembled KB/S composite. Assembled KB had a (002) peak at 23.6° and (101) peak at 43.2° , respectively. The interlayer distance of assembled KB is approximately 0.38 nm calculated by Bragg's law, which is slightly higher than that of graphite (0.34 nm). The good conductivity of KB mainly come from its graphitic domain. The XRD spectrum of assembled KB/S composite is similar to that of pure sulfur, indicating no phase change of sulfur occurred during in-situ precipitation in the pores of assembled KB.

Figure 6.6 shows the cross-section SEM image of assembled KB/sulfur composite cathode. It can be seen that the as-prepared cathode had a thickness of 150 nm and was packed without any cracks. Generally, cracks are formed during thick electrode coating of nanomaterial-containing slurry because the porous structure of nanomaterials can hold a large amount of solvents, which are evaporated in the subsequent drying process and results in collapse. The hierarchical structure of the assembled KB could be the main reason for this thick and compact sulfur cathode with a sulfur loading of 8.5 mg cm^{-2} . Specifically, the nanostructure of primary individual KB particle offers high surface area, leading to high sulfur loading. Meanwhile, the micro-sized morphology of assembled KB particles ensure good interconnection and mitigate the effect of volume shrinkage during slurry drying.

6.3.2 Titanium Nitride/Carbon Interlayer

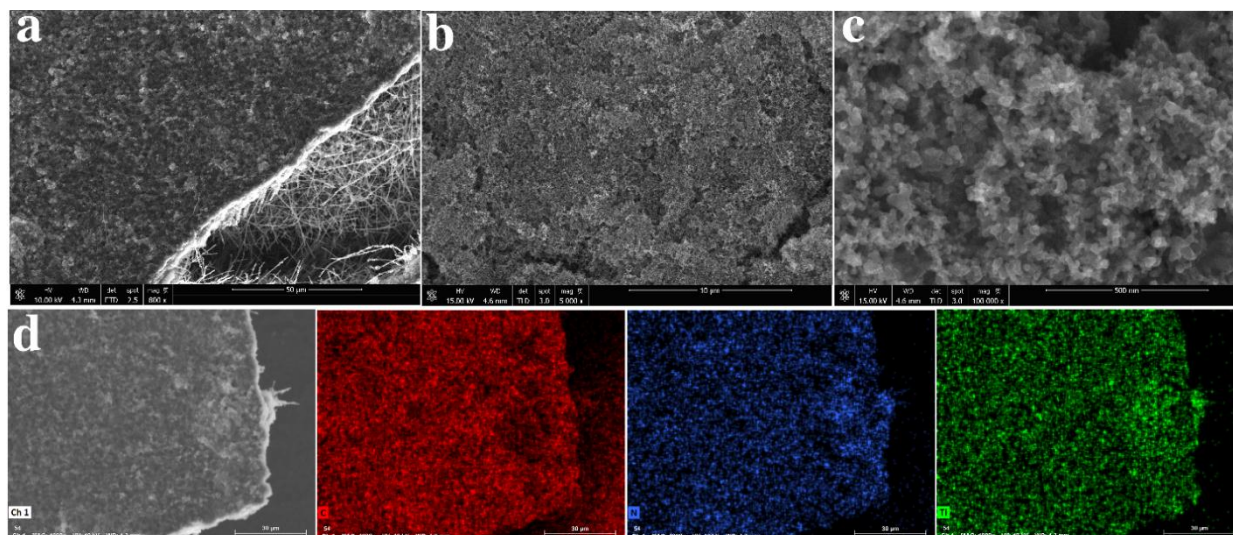


Figure 6.7: (a, b) Low and c) High Magnification SEM Images of TiN/C Interlayer and (d) Elemental Mapping.

A dual-interlayer consisting of titanium nitride (TiN) and carbon (C) fiber was readily prepared by using a facile doctor blade method. To characterize its microstructure, SEM was conducted. **Figure 6.7a and 6.7b** shows the top-view SEM images of TiN/C interlayer. From the low magnification images, it can be seen that TiN layer was uniformly coated on the surface of carbon fiber and had a porous structure, which is attributed to the slow evaporation of solvent during the drying process and a suitable binder ratio. Closer observation with SEM reveals that the average particle size of TiN is around 20 nm and particles are connected with each other to form a network. **(Figure 6.7c)** Because of the polarity difference, TiN particles can not infiltrate into the inner pores of carbon fiber, leading to the formation of a dual interlayer. The polar TiN layer can act as a chemical barrier to bind short-chain polysulfides (Li_2S_x , $1 < x < 4$) or lithium sulfide (Li_2S), whereas the non-polar carbon fiber layer serve as a secondary barrier and had an affinity to sulfur and long-chain polysulfides (Li_2S_x , $4 < x < 8$). ESD mapping was performed over the surface of TiN/C interlayer as shown in **Figure 6.7d**. Titanium and nitrogen signals are detected along with carbon, further confirming the uniform coating of TiN on the carbon nanofiber mat.

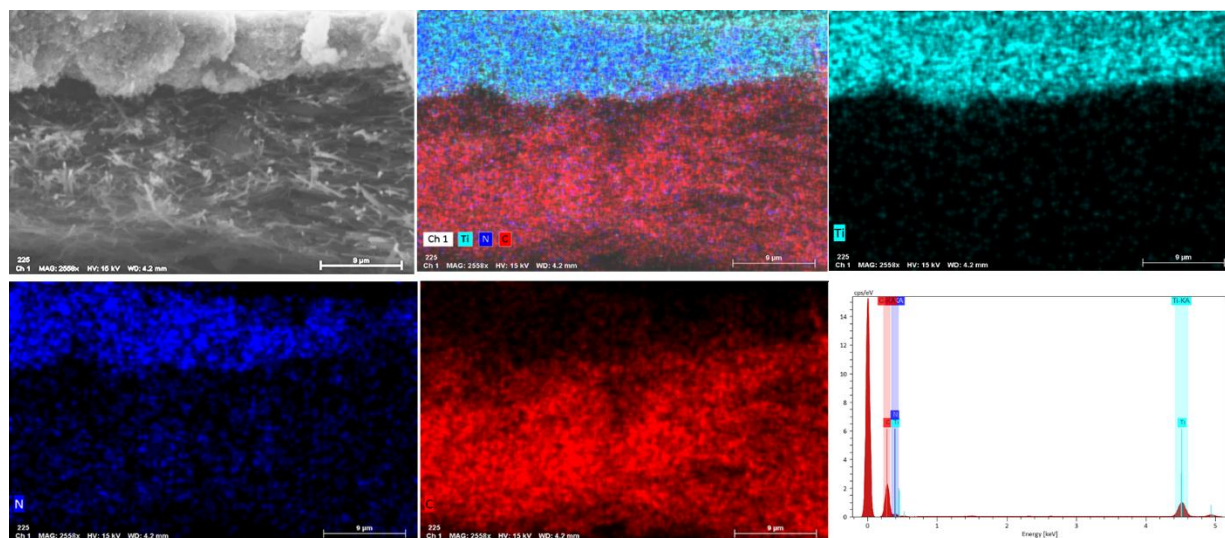


Figure 6.8: The Cross-Sectional SEM Images of TiN/C Interlayer and the Corresponding EDS Mapping and Spectrum.

Figure 6.8 shows the cross-sectional SEM images of TiN/C interlayer. The thickness of the TiN layer is determined to be approximately 10 μm , which is about one-third that of carbon nanofiber mat (30 μm). The corresponding EDS mapping clearly confirms the distribution of carbon, titanium and nitrogen in the dual-interlayer. In the EDS spectrum, only the mentioned three elements are detected, indicating the TiN/C interlayer is hardly oxidized in the air.

To investigate the structure of TiN/C composite, XRD and Raman spectroscopy were carried out. **Figure 6.9** shows the XRD pattern of the TiN/C interlayer, which matched well with that of pure TiN. Five typical peaks observed at 36.7° , 42.6° , 61.9° , 74.2° , and 78.1° are assigned to the face-centered cubic phase of TiN with lattice constant $a=0.422$ nm. The average crystallite size of the TiN particle was calculated to be 16 nm using Scherrer equation, which is in accordance with the SEM observation. In addition, a small broad peak observed around 25° is assigned to the (002) reflection of carbon nanofiber mat with a d-spacing of 0.36 nm. **Figure 6.10** shows the Raman spectrum of TiN/C interlayer. TiN exhibits four characteristic peaks at 153, 268, 404, and 606 cm^{-1} , which are caused by first-order transverse acoustic, longitudinal acoustic, second-order acoustic (2A), and transverse optical modes of TiN, respectively. In addition, the two peaks at ~ 1350 (D band) and $\sim 1593\text{ cm}^{-1}$ (G band) are related to the disorder and coplanar vibration of sp^2 -bonded carbon atoms in carbon nanofiber.

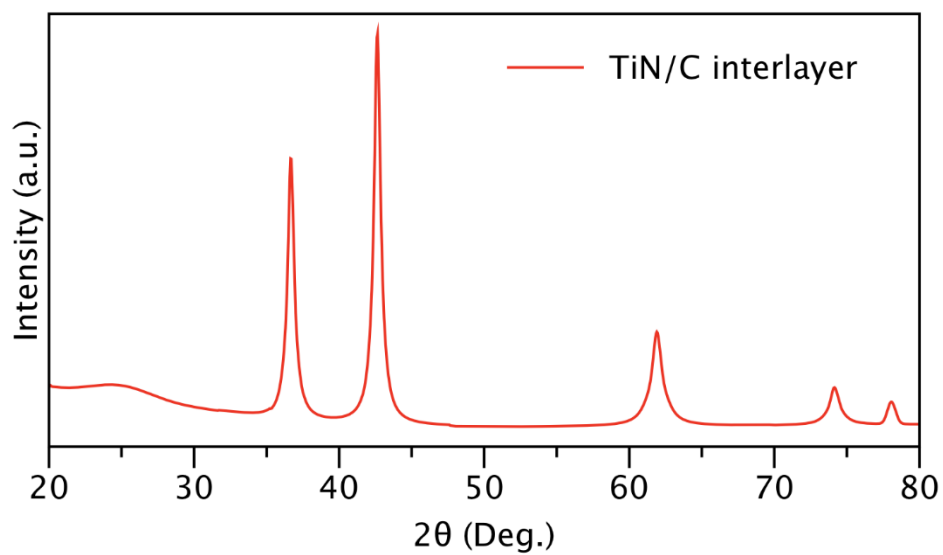


Figure 6.9: XRD Pattern of TiO₂/C Interlayer.

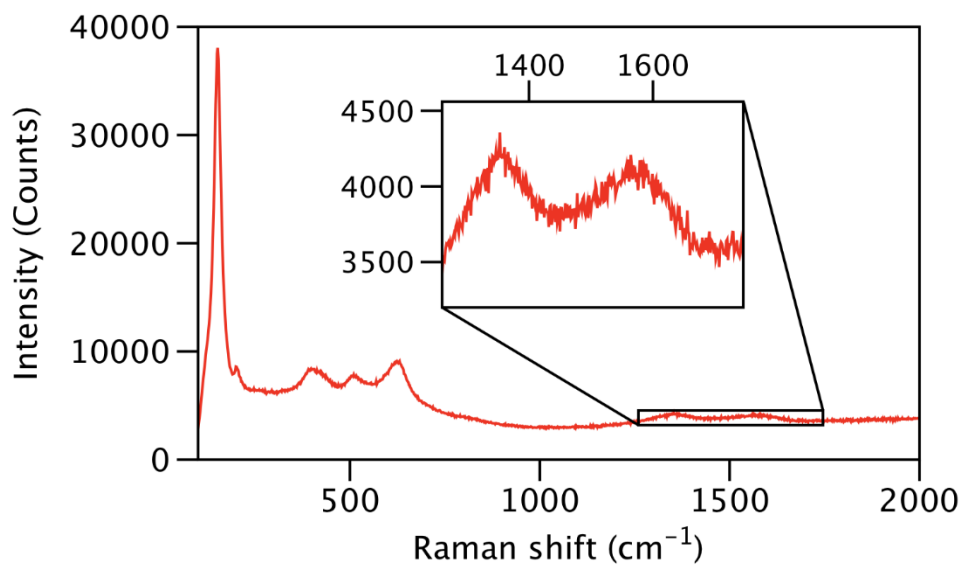


Figure 6.10: Raman Spectrum of TiN/C Interlayer.

6.4 Electrochemical Test and Postmortem Analysis

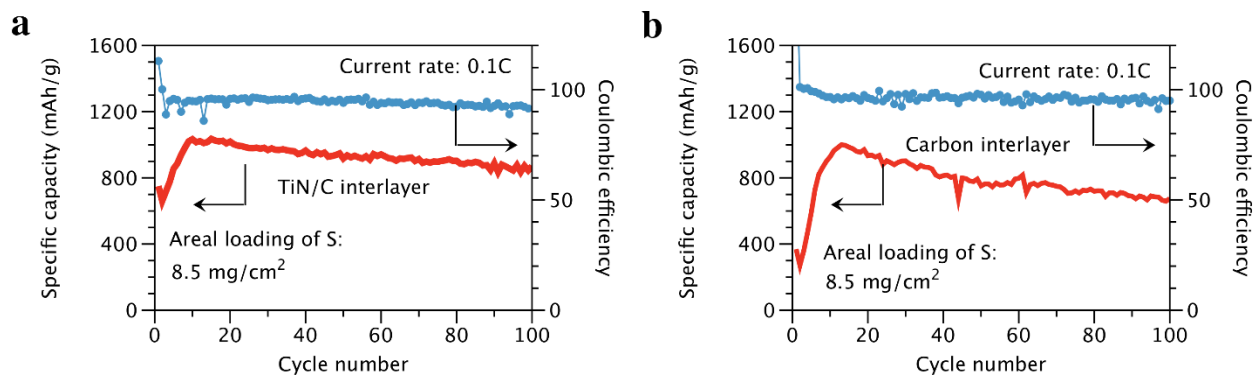


Figure 6.11: Cycle Performance of the Li-S Cell with Different Interlayers at a Current Rate of 0.1C: (a) TiN/C Interlayer; (b) Carbon Interlayer.

To investigate the effect of the TiN/C interlayer on electrochemical performance, the coin cells were assembled by using KB/S composite as cathode and lithium as anode. **Figure 6.11a and 6.11b** shows the cycle performance of the Li-S cell with different interlayers at a current rate of 0.1C. The cell with the TiN/C interlayer exhibited better capacity and cycle stability than the cell with the carbon interlayer. Because of the high S loading in the thick cathode, a low initial capacity of 750.2 and 396.4 mAh g⁻¹ were obtained for cell with TiN/C interlayer and cell with the carbon interlayer, respectively. The sulfur deeply buried in pores of the KB cannot be electrochemically used until it is exposed to the electrolyte. After several cycles, the capacity of both cells gradually increased due to the slow infiltration of electrolyte in the thick electrode. For the cell with TiN/C interlayer, it delivered the maximum capacity of 1033.5 mAh g⁻¹ at the 10th cycle and maintained a reversible capacity of 870.5 mAh g⁻¹ after 100 cycles, corresponding to a capacity decay rate of 0.17% per cycle. On the other hand, the reversible capacity of the cell with the carbon interlayer reached the highest of 982.3 mAh g⁻¹ at 10th cycles and then gradually decreased to 674.8 mAh g⁻¹ after 100 cycles with a capacity decay rate of approximately 0.35% per cycle. These results indicated that TiN can enhance the utilization of sulfur and improve the cycle stability.

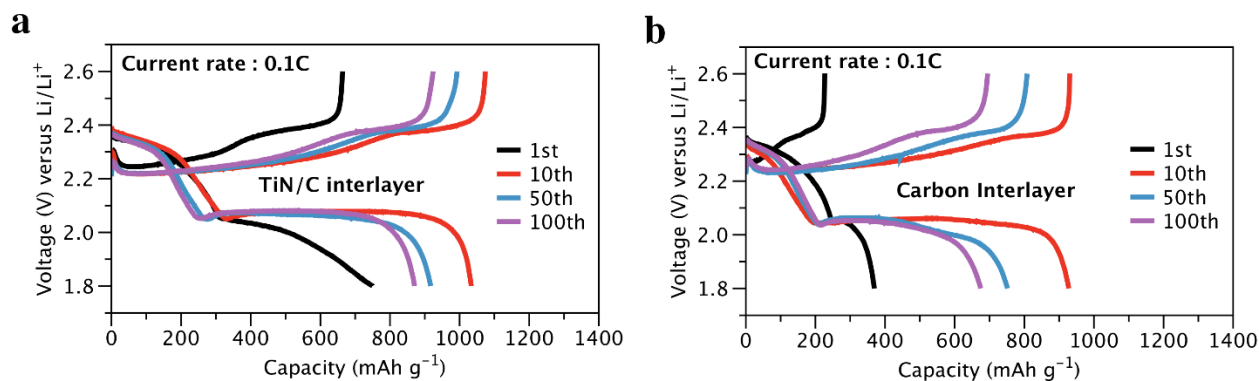


Figure 6.12: Discharge–Charge Profiles of the Li–S Cell with Different Interlayers at Current Rate of 0.1C: (a) TiN/C Interlayer; (b) Carbon Interlayer.

Figure 6.12a and 6.12b shows the galvanostatic charge/discharge profiles of the cathode with TiN/C interlayer and carbon interlayer in the 1st, 2nd, 10th, and 100th cycles. All curves exhibit two-plateau discharge behavior, corresponding to the formation of long-chain polysulfides at upper plateau and short-chain polysulfides at lower plateau. In the charge/discharge profile, cathode with TiN/C interlayer shows a much longer lower plateau than the cathode with carbon interlayer, indicating the TiN could facilitate the reduction of long-chain polysulfides to short-chain polysulfides.

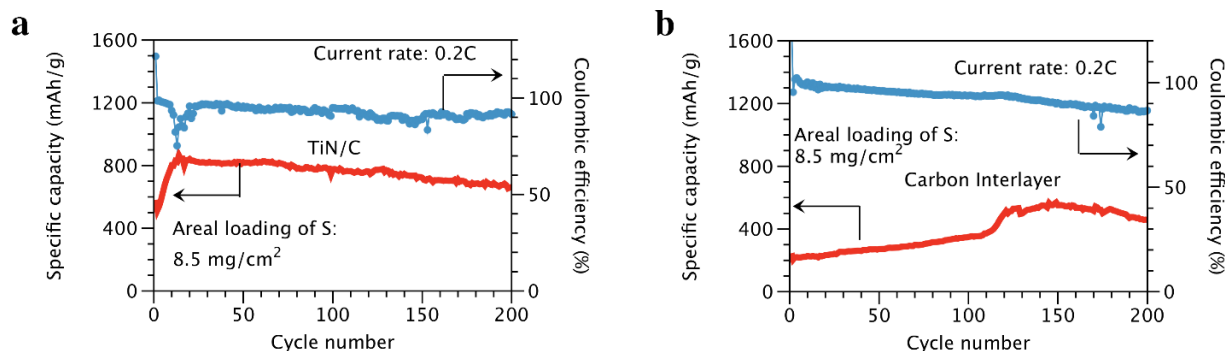


Figure 6.13: Cycle Performance of the Li–S Cell with Different Interlayers at a Current Rate of 0.2C: (a) TiN/C Interlayer; (b) Carbon Interlayer.

The cycle performance of the Li–S cell with different interlayers at a current rate of 0.2C was further compared. Significant improvement in capacity was achieved by TiN/C interlayer at a faster cell operation. When the current rate increased from 0.1 to 0.2C, the cell with TiN/C interlayer shows a similar trend in cycling (**Figure 6.13a**). The initial capacity of the cell with TiN/C interlayer was 581.3 mAh g⁻¹. After 14 cycles, the capacity increased to the highest of 864.2 mAh g⁻¹, which then slowly decreased to 663.5 mAh/g after 200 cycles with a capacity decay rate of 0.12% per cycle. In contrast, the cell with carbon interlayer delivered a much lower initial

capacity of 245.7 mAh g^{-1} at a current rate of 0.2C . Then it took almost 160 cycles for the cell with carbon interlayer to get activation and deliver the maximum capacity of 535 mAh g^{-1} . After 200 cycles, a reversible capacity of 458.2 mAh g^{-1} was retained, corresponding to a capacity decay rate of 0.35% per cycle (**Figure 6.13b**).

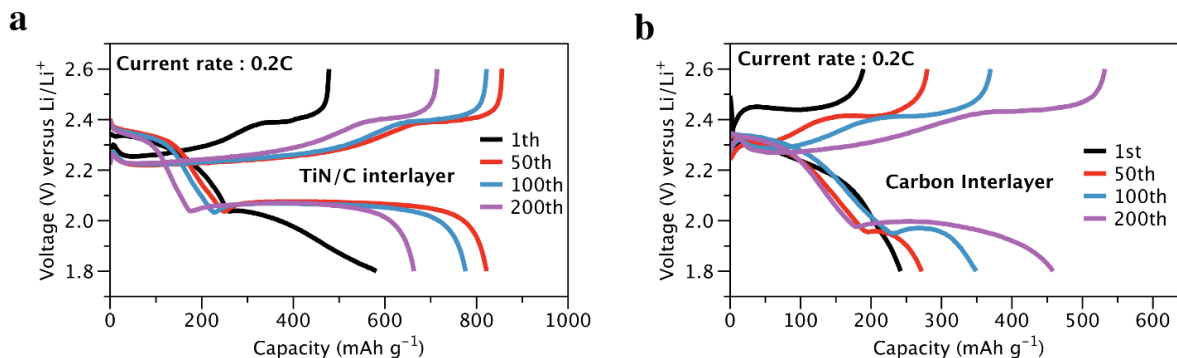


Figure 6.14: Discharge–Charge Profiles of the Li–S Cell with Different Interlayers at a Current Rate of 0.2C : (a) TiN/C Interlayer; (b) Carbon Interlayer.

Figure 6.14a and 6.14b shows the galvanostatic charge/discharge profiles of the cathode with TiN/C interlayer and carbon interlayer in the 1st, 2nd, 10th, and 100th cycles at a current rate of 0.2C . The cathode with TiN interlayer had much less polarization than the cathode with carbon interlayer, especially on the lower discharge plateau. The greatly enhanced reaction kinetics of the sulfur cathode with TiN/C interlayer could be ascribed to the accelerated fragmentation of long-chain polysulfides on TiN surface.

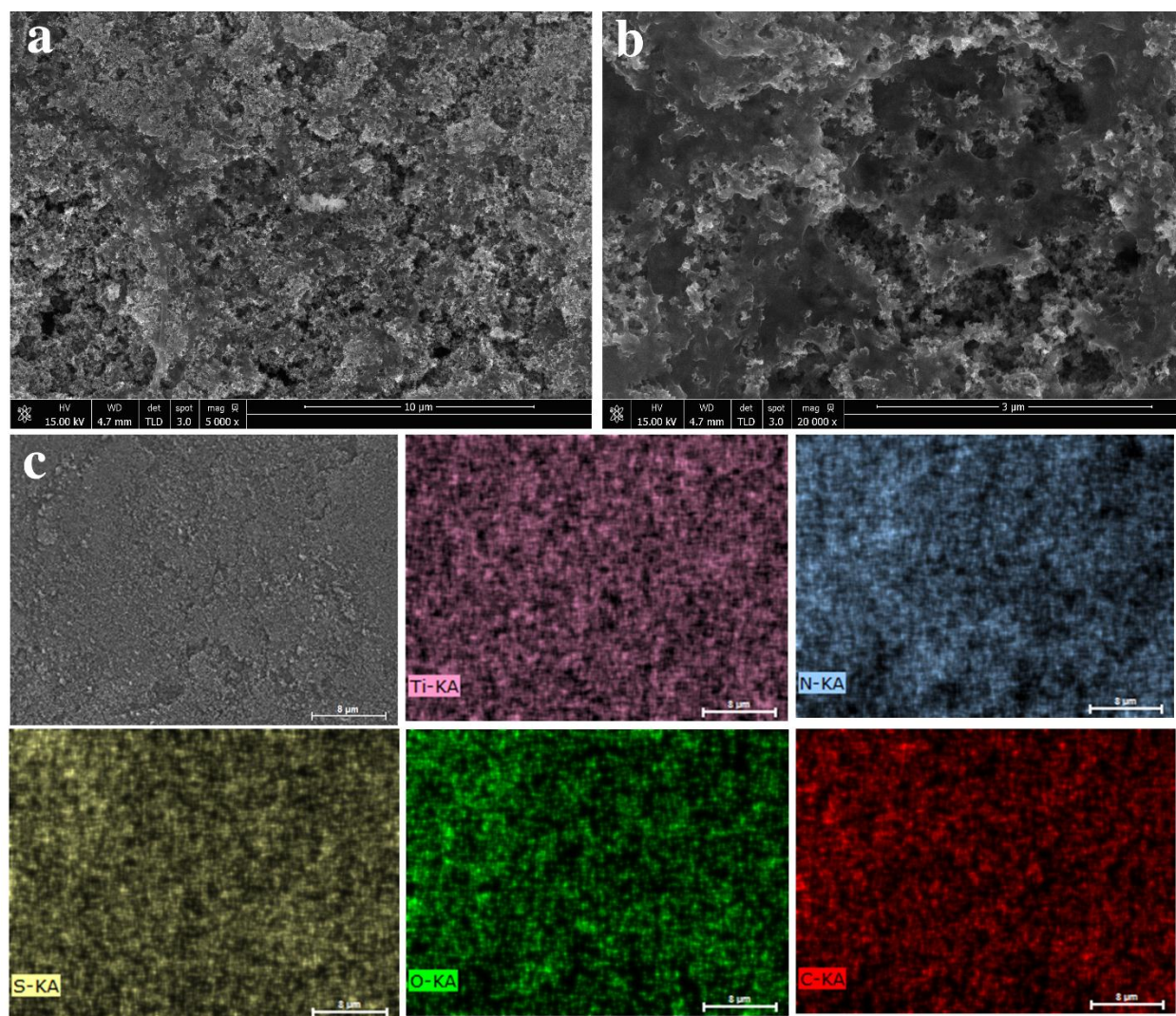


Figure 6.15: (a) Low and (b) High Magnification SEM Images of Cycled TiN/C Interlayer; (c) EDS Mapping of the Cycled TiN/C Interlayer.

After cycling, TiN/C interlayer was recovered from the coin cell and its morphology was characterized by SEM. From the low magnification SEM image (**Figure 6.15a**), it can be seen that the surface of TiN layer maintained intact and became much rougher. The magnified SEM (**Figure 6.15b**) further reveals a thin layer coating on the TiN nanoparticles, which was identified as sulfur species by the EDS mapping. The distribution of sulfur matches well with that of titanium and nitrogen (**Figure 6.15c**). These results suggest TiN layer provides favorable sites for the uniform deposition of solid sulfur species, which might be one reason for the enhanced reaction kinetics.

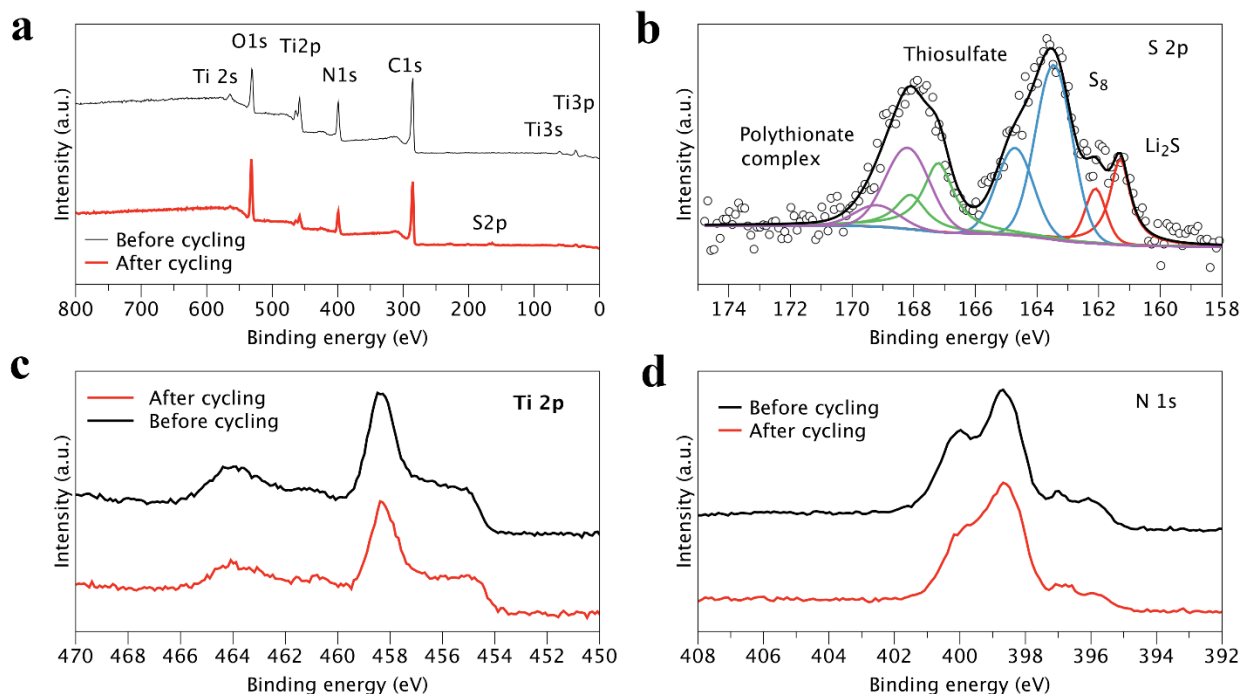


Figure 6.16 : (a) XPS Survey Spectra of TiO_2/C Interlayer before and after Cycling; (b) S_{2p} XPS Spectrum of The Cycled Interlayer; (c) Comparison of Ti_{2p} ; (d) N_{1s} XPS Spectrum of the Hybrid Interlayer before and after Cycling.

To investigate the chemical binding of sulfur species on the TiN layer, XPS was conducted on both the fresh and cycled TiN/C interlayer. After cycling, sulfur signal appeared in the survey spectrum, which is consistent with the above SEM observation (**Figure 6.16a**). The S_{2p} XPS spectrum as shown in **Figure 6.16b** reveals four sulfur species, including sulfur (S_8), Li_2S , thiosulfate and polythionate complex. These are similar solid sulfur species observed on the cycled metal-oxides based interlayer (TiO_2/C , ZnO/C) as previously described. It means TiN also plays a role in chemically adsorbing sulfur species. Based on the analysis of Ti_{2p} and N_{1s} spectrum before and after cycling (**Figure 6.16c** and **6.16d**), there is not obvious peak change in the Ti_{2p} , but a slightly change in the N_{1s} peak after cycling. It indicates the interaction mainly originated from the S-N bond, which is quite different from the Li-O bond between sulfur species and metal oxides.

6.5 Summary of this Chapter

In conclusion, a proof of concept for a dual interlayer was given. The hybrid interlayer was simply prepared by coating TiN nanoparticles on an electro-spun carbon nanofiber mats and was then sandwiched with a thick sulfur cathode. The polarity difference between TiN and carbon ensured the formation of a distinct two-layered structure of the interlayer. Meanwhile, the compact sulfur cathode with a high sulfur loading was achieved thanks to the hierarchical structure of the assembled carbon, which not only provided a high surface area but also accommodated the volume shrinkage during slurry drying process. The sulfur cathode with a dual TiN/C interlayer exhibited a much better sulfur utilization, cycle stability and rate performance than that with a pure C interlayer. It is demonstrated that TiN nanoparticles played a key role in chemically adsorbing polysulfides through a N-S bond. More importantly, it can catalyze the conversion of long-chain polysulfides to lithium sulfide during discharge, leading to the enhanced reaction kinetics. Moreover, carbon nanofiber mat offers mechanical support for the 10-um thick TiN film and acts as a physical barrier to block the diffusion of polysulfides to lithium anode. The fabrication of dual-interlayers consisting of polar metal-nitride nanoparticles and non-polar carbon fibers provides a facile approach to adsorption of polysulfides via chemical-physical interaction and electrocatalysis of their conversion reaction.

Chapter 7 Overall Conclusions and Future Directions

This final chapter outlines the overall conclusion of the research work carried out during my PhD project on the topic of “*Development of New Cathodic Interlayers with Nano-Architectures for Lithium-Sulfur Batteries*”, followed by the future research directions.

7.1 Conclusions

- A core-shell structured S/MWCNT composite cathode was prepared using a simple thermal infusion method. MWCNT acted as core and provided electron transfer path from and to the sulfur shell. There is no chemical interaction between MWCNT and S and no new phase was generated during the synthesis process. The thickness of S shell was around 30 nm and the total content of S in the composite was about 70% wt. In addition, the areal loading of sulfur in the cathode was 3 mg/cm². Without the incorporation of an interlayer, the S/MWCNT composite cathode exhibited severe capacity decay due to the direct contact of sulfur shell to electrolyte, which caused the dissolution of lithium polysulfide intermediates into the electrolyte and led to active materials loss.
- A brush-like ZnO nanowires/Ni foam interlayer was initially prepared ex-situ using a wet-chemistry method and was coupled with the as-obtained S/MWCNT composite cathode. It significantly improved the capacity and cycle stability of the S/MWCNT composite cathode attributed to the hierarchical structure of the interlayer. Ni foam provided extra reaction sites for migrating polysulfides and catalyzed the redox reaction during the reutilization process while ZnO nanowires grown on the Ni foam surface played a key role in adsorbing polysulfides via a strong Li-O bond. After the successful demonstration, electro-spun carbon nanofiber was fabricated to replace Ni foam in order to reduce the overweight of batteries. The S/MWCNT composite cathode with a ZnO/C interlayer exhibits a reversible capacity of 776 mA h g⁻¹ after 200 cycles at 1C with only 0.05% average capacity loss per cycle. The integration of well-organized ZnO nanowires with the conductive framework of carbon fiber afforded fast electron and ion motion for polysulfides adsorption and reutilization. The design of chemi-functional interlayers with brush-like nano-architecture opens a new direction for advancing high-performance Li-S batteries.

- A praline-like TiO_2 /carbon nanofiber interlayer was successfully synthesized in-situ by carbonizing a PVP/ TiO_2 precursor and was incorporated with the as-obtained S/MWCNT composite cathode. TiO_2 nanoparticles with a size gradient occupy both the surface (~ 30 nm) and the internal (< 10 nm) of the carbon fiber, which enables the chemisorption of polysulfides throughout a conductive nano-architecture. The porous conductive carbon backbone helps in the physical absorption of polysulfides and provides redox reaction sites to allow the polysulfides to be reused. More importantly, the flexibility and mechanical strength of the interlayer with 79 wt% TiO_2 loading can maintain the stability of this hierarchical structure and can also accommodate the volume variation arising from the conversion between polysulfide and sulfur during the re-utilization process. Taking advantage of the praline-like interlayer design, a S/MWCNT composite cathode with a TiO_2 /C nanofiber interlayer delivered a high reversible capacity of $1160.7 \text{ mAh g}^{-1}$ at a current rate of 0.2C and exhibited a good rate performance of 715.4 mAh g^{-1} at 1C.
- The derivatives of TiO_2 /C nanofibers were synthesized by changing PVP precursor concentration and carbonization temperature. It was found that higher PVP concentration contributed to thicker diameters of the as-spun nanofibers and smaller grain size of TiO_2 nanoparticles after carbonization at 800°C . Carbon derived from the PVP during carbonization inhibited the sinter and growth of TiO_2 nanocrystals. Moreover, carbonization temperature directly determined the phase of TiO_2 nanoparticles in the nanofibers. As the temperature increased from 800 to 1000°C , the rutile phase TiO_2 was gradually transferred to $\text{TiO}_{1-x}\text{N}_x$ with a cubic rock-salt structure.
- A assembled KB/S composite cathode was prepared using a wet-chemistry method. The assembled KB has a high surface area and an oval-like microstructure, which afforded a S content of 90 wt% and enabled a pinhole-free cathode with an areal sulfur loading as high as 8.5 mg cm^{-2} . The pores of the assembled KB was completely filled up by crystalline sulfur. In addition, the inter-particle contact of the assembled KB provided fast electron transfer path and ensured structure stability. More importantly, the internal space of the oval-like microstructure can not only hold electrolyte, but also accommodate volume change of S species during charging and discharging. This composite cathode is very promising for practical application.

- A dual interlayer consisting of TiN nanoparticles and carbon nanofibers was prepared and was sandwiched with the as-obtained assembled KB/S composite cathode with a high S loading. Compared with the cathode with pure carbon interlayer, the one with the TiN/C interlayer exhibited much better capacity and rate performance, which are mainly attributed to the good conductivity of TiN and its electrocatalysis of polysulfide conversion. In addition, TiN also played a role in chemically adsorbing polysulfides via a N-S bond, enhancing the cycle stability of the cathode.

In conclusion, cathode-interlayer couples with different sulfur loading and nanostructure design were fabricated for Li-S batteries. It was found that the interlayers consisting of a polar component (ZnO, TiO₂, TiN) and a conductive framework (Ni foam, electro-spun carbon nanofiber) can successfully improve the performance of the cathodes (S/MWCNT, S/assembled KB composite) by effectively adsorbing migrating polysulfides via a strong chemical bond (Li-O, N-S) and making them electrochemical reusable. These findings provide a new strategy to design functional interlayers for high-performance cathodes. For lab-based study, the cathode could have a low sulfur loading and is coupled with a fine structured (brush-like, praline-like) interlayer, whereas, the cathode with a high sulfur loading and a simple dual structured interlayer has the potential for industrial production.

7.2 Future Directions

- Further optimization of the sulfur loading in cathode and the thickness of interlayer could make the system work more efficiently. For example, by systematically increasing the sulfur loading of cathode, the upper limit for the interlayer can be discovered.
- It would be very interesting to investigate other morphologies in the nanostructured ZnO based interlayer, such as nanoplates or nano-ribbons. These morphologies of ZnO are developed by tuning the growth rate along specific directions and thus have different polar surface, which might affect the chemical adsorption of polysulfides. The pore structure of ZnO is another important factor to be considered because it could enlarge the diffusion path of polysulfides. MOF derived ZnO materials with high surface area and unique pore structures are promising candidates for further study.

- Further optimization of TiO_2 ratio in the TiO_2/C might improve the conductivity of the composite and thus enhance the utilization of adsorbed polysulfides. Doping of TiO_2 might improve its chemical interaction with polysulfides. In addition, titanium oxynitride/carbon is also a potential chemi-functional interlayer because titanium oxynitride has nitrogen and oxygen, both of which might bond with polysulfides.
- Tuning the weight ratio of the two components of the dual interlayer could find a balance between the physical and chemical interaction, thus improving the adsorption process of polysulfides. Although a proof of concept for the dual interlayer has been successfully given, it is still necessary to reduce its thickness and weight to enhance the overall energy density of the cell for practical application. In fact, based on the concept of the dual interlayer, a huge amount of work could be done by simply changing the combination of materials for the interlayer. For example, a potential dual interlayer could be made of sulfides and carbon because some sulfides like Co_3S_4 also have moderate interaction with polysulfides. Moreover, the dual interlayer can be applied to any sulfur cathodes.

Bibliography

- [1] D. A. J. Rand, "A Journey on the Electrochemical Road to Sustainability," *J. Solid State Electrochem.*, vol. 15, pp. 1579-1622, 2011.
- [2] M. Winter and R. J. Brodd, "What Are Batteries, Fuel Cells, and Supercapacitors?," *Chem. Rev.*, vol. 104, pp. 4245-4270, 2004.
- [3] D. Larcher and J. M. Tarascon, "Towards Greener and More Sustainable Batteries for Electrical Energy Storage," *Nat. Chem*, vol. 7, pp. 19-29, 2014.
- [4] B. Scrosati, J. Hassoun, and Y.-K. Sun, "Lithium-ion Batteries. A Look into the Future," *Energy Environ. Sci.*, vol. 4, pp. 3287-3295, 2011.
- [5] J. W. Choi and D. Aurbach, "Promise and Reality of Post-Lithium-Ion Batteries With High Energy Densities," *Nat. Rev. Mater.*, vol. 1, p. 16013, 2016.
- [6] Z. W. Seh, Y. Sun, Q. Zhang, and Y. Cui, "Designing High-Energy Lithium–Sulfur Batteries," *Chem, Soc. Rev.*, vol. 45, pp. 5605-5634, 2016.
- [7] M. Armand and J. M. Tarascon, "Building Better Batteries," *Nature*, vol. 451, pp. 652-657, 2008.
- [8] R. Van Noorden, "The Rechargeable Revolution: A Better Battery," *Nature*, vol. 507, pp. 26-28, 2014.
- [9] X.-P. Gao and H.-X. Yang, "Multi-Electron Reaction Materials for High Energy Density Batteries," *Energy Environ. Sci.*, vol. 3, pp. 174-189, 2010.
- [10] B. Scrosati and J. Garche, "Lithium batteries: Status, prospects and future," *Journal of Power Sources*, vol. 195, pp. 2419-2430, 2010.
- [11] X. Fang and H. Peng, "A Revolution In Electrodes: Recent Progress In Rechargeable Lithium-Sulfur Batteries," *Small*, vol. 11, pp. 1488-1511, 2015.
- [12] X. Ji and L. F. Nazar, "Advances in Li–S Batteries," *J. Mater. Chem.*, vol. 20, pp. 9821-9826, 2010.
- [13] H. Yamin, A. Gorenshtein, J. Penciner, Y. Sternberg, and E. Peled, "Lithium Sulfur Battery: Oxidation/Reduction Mechanisms of Polysulfides in THF Solutions," *J. Electrochem. Soc.*, vol. 135, pp. 1045-1048, 1988.
- [14] E. Peled, Y. Sternberg, A. Gorenshtein, and Y. Lavi, "Lithium-Sulfur Battery: Evaluation of Dioxolane-Based Electrolytes," *J. Electrochem. Soc.*, vol. 136, pp. 1621-1625, 1989.
- [15] H. Yamin and E. Peled, "Electrochemistry of a Nonaqueous Lithium/Sulfur Cell," *Journal of Power Sources*, vol. 9, pp. 281-287, 1983.

- [16] D.-R. Chang, S.-H. Lee, S.-W. Kim, and H.-T. Kim, "Binary Electrolyte Based on Tetra(Ethylene Glycol) Dimethyl Ether and 1,3-Dioxolane for Lithium–Sulfur Battery," *Journal of Power Sources*, vol. 112, pp. 452-460, 2002.
- [17] S. Kim, Y. Jung, and H. S. Lim, "The Effect of Solvent Component on the Discharge Performance of Lithium–Sulfur Cell Containing Various Organic Electrolytes," *Electrochimica Acta*, vol. 50, pp. 889-892, 2004.
- [18] J.-W. Park, K. Ueno, N. Tachikawa, K. Dokko, and M. Watanabe, "Ionic Liquid Electrolytes for Lithium–Sulfur Batteries," *J. Phys. Chem. C*, vol. 117, pp. 20531-20541, 2013.
- [19] X.-G. Sun, X. Wang, R. T. Mayes, and S. Dai, "Lithium–Sulfur Batteries Based on Nitrogen-Doped Carbon and an Ionic-Liquid Electrolyte," *ChemSusChem*, vol. 5, pp. 2079-2085, 2012.
- [20] J.-W. Park, K. Yamauchi, E. Takashima, N. Tachikawa, K. Ueno, K. Dokko and M. Watanabe, "Solvent Effect of Room Temperature Ionic Liquids on Electrochemical Reactions in Lithium–Sulfur Batteries," *J. Phys. Chem. C*, vol. 117, pp. 4431-4440, 2013.
- [21] Y. Yang, G. Y. Zheng, and Y. Cui, "Nanostructured Sulfur Cathodes," *Chem. Soc. Rev.*, vol. 42, pp. 3018-3032, 2013.
- [22] J.-Q. Huang, Q. Zhang, and F. Wei, "Multi-Functional Separator/Interlayer System for High-Stable Lithium-Sulfur Batteries: Progress and Prospects," *Energy Storage Materials*, vol. 1, pp. 127-145, 2015.
- [23] S. Xin, Y.-G. Guo, and L.-J. Wan, "Nanocarbon Networks for Advanced Rechargeable Lithium Batteries," *Acc. Chem. Res.*, vol. 45, pp. 1759-1769, 2012.
- [24] J. S. Lee, J. Jun, J. Jang, and A. Manthiram, "Sulfur-Immobilized, Activated Porous Carbon Nanotube Composite Based Cathodes for Lithium-Sulfur Batteries," *Small*, vol. 13, p. 1602984, 2017.
- [25] S. Rehman, X. Gu, K. Khan, N. Mahmood, W. Yang, X. Huang, S. J. Guo and Y. L. Hou, "3D Vertically Aligned and Interconnected Porous Carbon Nanosheets as Sulfur Immobilizers for High Performance Lithium-Sulfur Batteries," *Adv. Energy Mater.*, vol. 6, p.1502518, 2016.
- [26] C. Li and L. Yin, "Sulfur Immobilized in Hierarchically Porous Structured Carbon as Cathodes for Lithium-Sulfur Battery with Improved Electrochemical Performance," *Part. Part. Syst. Charact.*, vol. 32, pp. 756-763, 2015.
- [27] X. Yang, N. Yan, W. Zhou, H. Zhang, X. Li, and H. Zhang, "Sulfur Embedded in One-Dimensional French Fries-Like Hierarchical Porous Carbon Derived from a Metal–Organic Framework for High Performance Lithium–Sulfur Batteries," *J. Mater. Chem. A*, vol. 3, pp. 15314-15323, 2015.
- [28] X. Zhao, Y. Liu, J. Manuel, G. S. Chauhan, H.-J. Ahn, K.-W. Kim, K. K. Cho and J. H. Ahn, "Nitrogen-Doped Mesoporous Carbon: A Top-Down Strategy to Promote Sulfur Immobilization for Lithium-Sulfur Batteries," *ChemSusChem*, vol. 8, pp. 3234-3241, 2015.

- [29] X. Ye, J. Ma, Y.-S. Hu, H. Wei, and F. Ye, "MWCNT Porous Microspheres with an Efficient 3D Conductive Network for High Performance Lithium–Sulfur Batteries," *J. Mater. Chem. A*, vol. 4, pp. 775-780, 2016.
- [30] M.-Q. Zhao, H.-J. Peng, G.-L. Tian, Q. Zhang, J.-Q. Huang, X.-B. Cheng, C. Tang and F. Wei, "Hierarchical Vine-Tree-Like Carbon Nanotube Architectures: In-Situ CVD Self-Assembly and Their Use as Robust Scaffolds for Lithium-Sulfur Batteries," *Adv. Mater.*, vol. 26, pp. 7051-7058, 2014.
- [31] Z. Yuan, H.-J. Peng, J.-Q. Huang, X. Y. Liu, D.-W. Wang, X.-B. Cheng and Q. Zhang, "Hierarchical Free-Standing Carbon-Nanotube Paper Electrodes with Ultrahigh Sulfur-Loading for Lithium-Sulfur Batteries," *Adv. Funct. Mater.*, vol. 24, pp. 6105-6112, 2014.
- [32] J. C. Guo, Y. H. Xu, and C. S. Wang, "Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium-Sulfur Batteries," *Nano Lett.*, vol. 11, pp. 4288-4294, 2011.
- [33] S.-C. Han, M.-S. Song, H. Lee, H.-S. Kim, H.-J. Ahn, and J.-Y. Lee, "Effect of Multiwalled Carbon Nanotubes on Electrochemical Properties of Lithium/Sulfur Rechargeable Batteries," *J. Electrochem. Soc.*, vol. 150, pp. A889-A893, 2003.
- [34] R. Fang, S. Zhao, S. Pei, X. Qian, P.-X. Hou, H.-M. Cheng, C. Liu and F. Li, "Toward More Reliable Lithium–Sulfur Batteries: An All-Graphene Cathode Structure," *ACS Nano*, vol. 10, pp. 8676-8682, 2016.
- [35] B. Li, S. Li, J. Liu, B. Wang, and S. Yang, "Vertically Aligned Sulfur–Graphene Nanowalls on Substrates for Ultrafast Lithium–Sulfur Batteries," *Nano Lett.*, vol. 15, pp. 3073-3079, 2015.
- [36] C. Zhang, D.-H. Liu, W. Lv, D.-W. Wang, W. Wei, G.-M. Zhou, S. Wang, F. Li, B. H. Li, F. Kang and Q. H. Yang, "A High-Density Graphene-Sulfur Assembly: A Promising Cathode for Compact Li-S Batteries," *Nanoscale*, vol. 7, pp. 5592-5597, 2015.
- [37] G. Zhou, L. Li, C. Ma, S. Wang, Y. Shi, N. Koratkar, W. Ren, F. Li and H. M. Chen, "A Graphene Foam Electrode with High Sulfur Loading for Flexible and High Energy Li-S Batteries," *Nano Energy*, vol. 11, pp. 356-365, 2015.
- [38] G. M. Zhou, E. Paek, G. S. Hwang, and A. Manthiram, "Long-Life Li/Polysulphide Batteries with High Sulphur Loading Enabled by Lightweight Three-Dimensional Nitrogen/Sulphur-Codoped Graphene Sponge," *Nat. Commun.*, vol. 6, p. 7760, 2015.
- [39] Y. Qiu, W. Li, W. Zhao, G. Li, Y. Hou, M. Liu, L. Zhou, F. Ye, H. Li, Z. Wei, S. Yang, W. Duan, Y. Ye, J. Guo and Y. Zhang., "High-Rate, Ultralong Cycle-Life Lithium/Sulfur Batteries Enabled by Nitrogen-Doped Graphene," *Nano Lett.*, vol. 14, pp. 4821-4827, 2014.
- [40] T. Lin, Y. Tang, Y. Wang, H. Bi, Z. Liu, F. Huang, X. Xie and M. Jiang, "Scotch-Tape-Like Exfoliation of Graphite Assisted with Elemental Sulfur and Graphene–Sulfur Composites for High-Performance Lithium-Sulfur Batteries," *Energy Environ. Sci.*, vol. 6, pp. 1283-1290, 2013.
- [41] F. Pei, T. An, J. Zang, X. Zhao, X. Fang, M. Zheng, Q. Dong, N. Zheng, "From Hollow Carbon Spheres to N-Doped Hollow Porous Carbon Bowls: Rational Design of Hollow Carbon Host for Li-S Batteries," *Adv. Energy Mater.*, vol. 6, pp. 1502539, 2016.

- [42] Y. Zhong, S. Wang, Y. Sha, M. Liu, R. Cai, L. Li and Z. Shao, "Trapping Sulfur in Hierarchically Porous, Hollow Indented Carbon Spheres: A High-Performance Cathode for Lithium–Sulfur Batteries," *J. Mater. Chem. A*, vol. 4, pp. 9526-9535, 2016.
- [43] W. Zhou, C. Wang, Q. Zhang, H. D. Abruña, Y. He, J. Wang, S. X. Mao and X. Xiao "Tailoring Pore Size of Nitrogen-Doped Hollow Carbon Nanospheres for Confining Sulfur in Lithium-Sulfur Batteries," *Adv. Energy Mater.*, vol. 5, pp. 1401752, 2015.
- [44] J. Zang, T. An, Y. Dong, X. Fang, M. Zheng, Q. Dong and N. Zheng, "Hollow-in-Hollow Carbon Spheres with Hollow Foam-Like Cores for Lithium–Sulfur Batteries," *Nano Res.*, vol. 8, pp. 2663-2675, 2015.
- [45] G. M. Zhou, Y. B. Zhao, and A. Manthiram, "Dual-Confined Flexible Sulfur Cathodes Encapsulated in Nitrogen-Doped Double-Shelled Hollow Carbon Spheres and Wrapped with Graphene for Li-S Batteries," *Adv. Energy Mater.*, vol. 5, p. 1402263, 2015.
- [46] S. Chen, X. Huang, B. Sun, J. Zhang, H. Liu, and G. Wang, "Multi-Shelled Hollow Carbon Nanospheres for Lithium–Sulfur Batteries with Superior Performances," *J. Mater. Chem. A*, vol. 2, pp. 16199-16207, 2014.
- [47] J. He, Y. Chen, P. Li, F. Fu, Z. Wang, and W. Zhang, "Three-Dimensional CNT/Graphene–Sulfur Hybrid Sponges with High Sulfur Loading as Superior-Capacity Cathodes for Lithium–Sulfur Batteries," *J. Mater. Chem. A*, vol. 3, pp. 18605-18610, 2015.
- [48] S. Lu, Y. Cheng, X. Wu, and J. Liu, "Significantly Improved Long-Cycle Stability in High-Rate Li-S Batteries Enabled by Coaxial Graphene Wrapping over Sulfur-Coated Carbon Nanofibers," *Nano Lett.*, vol. 13, pp. 2485-2489, 2013.
- [49] X. a. Chen, Z. Xiao, X. Ning, Z. Liu, Z. Yang, C. Zou, S. Wang, X. Chen, Y. Chen and S. Huang, "Sulfur-Impregnated, Sandwich-Type, Hybrid Carbon Nanosheets with Hierarchical Porous Structure for High-Performance Lithium-Sulfur Batteries," *Adv. Energy Mater.*, vol. 4, pp. 1301988, 2014.
- [50] G. Zhou, Y. Zhao, and A. Manthiram, "Dual-Confined Flexible Sulfur Cathodes Encapsulated in Nitrogen-Doped Double-Shelled Hollow Carbon Spheres and Wrapped with Graphene for Li-S Batteries," *Adv. Energy Mater.*, vol. 5, pp. 1402263, 2015.
- [51] H. Hu, H. Cheng, Z. Liu, G. Li, Q. Zhu and Y. Yu, "In Situ Polymerized PAN-Assisted S/C Nanosphere with Enhanced High-Power Performance as Cathode for Lithium/Sulfur Batteries," *Nano Lett.*, vol. 15, pp. 5116-5123, 2015.
- [52] Y. Fu and A. Manthiram, "Orthorhombic Bipyramidal Sulfur Coated with Polypyrrole Nanolayers As a Cathode Material for Lithium–Sulfur Batteries," *J. Phys. Chem. C*, vol. 116, pp. 8910-8915, 2012.
- [53] Y. Yang, G. Yu, J. J. Cha, H. Wu, M. Vosgueritchian, Y. Yao, Z. Bao and Y. Cui, "Improving the Performance of Lithium-Sulfur Batteries by Conductive Polymer Coating," *ACS Nano*, vol. 5, pp. 9187-9193, 2011.
- [54] X. Liang, M. Zhang, M. R. Kaiser, X. Gao, K. Konstantinov, R. Tandiono, Z. Wang, H.-K. Liu, S.-X. Dou and J. Wang, "Split-Half-Tubular Polypyrrole@Sulfur@Polypyrrole

- Composite with a Novel Three-Layer-3D Structure as Cathode for Lithium/Sulfur Batteries," *Nano Energy*, vol. 11, pp. 587-599, 2015.
- [55] L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M. H. Engelhard, L. V. Saraf, Z. Nie, G. J. Exarhos and Jun Liu, "A Soft Approach to Encapsulate Sulfur: Polyaniline Nanotubes for Lithium-Sulfur Batteries with Long Cycle Life," *Adv. Mater.*, vol. 24, pp. 1176-1181, 2012.
- [56] W. Li, Q. Zhang, G. Zheng, Z. W. Seh, H. Yao, and Y. Cui, "Understanding the Role of Different Conductive Polymers in Improving the Nanostructured Sulfur Cathode Performance," *Nano Lett.*, vol. 13, pp. 5534-5540, 2013.
- [57] H. Kim, J. Lee, H. Ahn, O. Kim, and M. J. Park, "Synthesis of Three-Dimensionally Interconnected Sulfur-Rich Polymers for Cathode Materials of High-Rate Lithium-Sulfur Batteries," *Nat. Commun.*, vol. 6, p. 7278, 2015.
- [58] Z. Li, J. Zhang, B. Guan, D. Wang, L.-M. Liu, and X. W. D. Lou, "A Sulfur Host Based on Titanium Monoxide@Carbon Hollow Spheres for Advanced Lithium-Sulfur Batteries," *Nat. Commun.*, vol. 7, p. 13065, 2016.
- [59] S. Rehman, S. Guo, and Y. Hou, "Rational Design of Si/SiO₂ @Hierarchical Porous Carbon Spheres as Efficient Polysulfide Reservoirs for High-Performance Li-S Battery," *Adv. Mater.*, vol. 28, pp. 3167-3172, 2016.
- [60] M. Yu, J. Ma, H. Song, A. Wang, F. Tian, Y. Wang, H. Qiu and R. Wang, "Atomic Layer Deposited TiO₂ On a Nitrogen-Doped Graphene/Sulfur Electrode for High Performance Lithium-Sulfur Batteries," *Energy Environ. Sci.*, vol. 9, pp. 1495-1503, 2016.
- [61] Z. Zhang, Q. Li, S. Jiang, K. Zhang, Y. Lai, and J. Li, "Sulfur Encapsulated in a TiO₂-Anchored Hollow Carbon Nanofiber Hybrid Nanostructure for Lithium-Sulfur Batteries," *Chem. Eur. J.*, vol. 21, pp. 1343-1349, 2015.
- [62] X. Liang, C. Y. Kwok, F. Lodi-Marzano, Q. Pang, M. Cuisinier, H. Huang, C. J. Hart, D. Houtarde, K. Kaup, H. Sommer, T. Brezesinski, J. Janek and L. F. Naza , "Tuning Transition Metal Oxide-Sulfur Interactions for Long Life Lithium Sulfur Batteries: The "Goldilocks" Principle," *Adv. Energy Mater.*, vol. 6, p. 1501636, 2015.
- [63] X. Tao, J. Wang, Z. Ying, Q. Cai, G. Zheng, Y. Gan, H. Huang, Y. Xia, C. Liang, W. Zhang and Y. Cui., "Strong Sulfur Binding with Conducting Magnéli-Phase Ti_nO_{2n-1} Nanomaterials for Improving Lithium-Sulfur Batteries," *Nano Lett.*, vol. 14, pp. 5288-5294, 2014.
- [64] M. Liu, F. Ye, W. Li, H. Li, and Y. Zhang, "Chemical Routes Toward Long-Lasting Lithium/Sulfur Cells," *Nano Res.*, vol. 9, pp. 94-116, 2016.
- [65] R. Singhal, S.-H. Chung, A. Manthiram, and V. Kalra, "A Free-Standing Carbon Nanofiber Interlayer for High-Performance Lithium-Sulfur Batteries," *J. Mater. Chem. A*, vol. 3, pp. 4530-4538, 2015.
- [66] J. Balach, T. Jaumann, M. Klose, S. Oswald, J. Eckert, and L. Giebeler, "Mesoporous Carbon Interlayers with Tailored Pore Volume as Polysulfide Reservoir for High-Energy Lithium-Sulfur Batteries," *J. Phys. Chem. C*, vol. 119, pp. 4580-4587, 2015.

- [67] R. Singhal, S.-H. Chung, A. Manthiram, and V. Kalra, "A Free-Standing Carbon Nanofiber Interlayer for High-Performance Lithium–Sulfur Batteries," *J. Mater. Chem. A*, vol. 3, pp. 4530-4538, 2015.
- [68] S.-H. Chung and A. Manthiram, "A Hierarchical Carbonized Paper with Controllable Thickness as a Modulable Interlayer System for High Performance Li–S Batteries," *Chem. Commun.*, vol. 50, pp. 4184-4187, 2014.
- [69] C. Zu, Y.-S. Su, Y. Fu, and A. Manthiram, "Improved Lithium–Sulfur Cells with a Treated Carbon Paper Interlayer," *Phys. Chem. Chem. Phys.*, vol. 15, pp. 2291-2297, 2013.
- [70] Q. Li, M. Liu, X. Qin, J. Wu, W. Han, G. Liang, D. Zhou, Y. -B. He, B. Li and F. Kang "Cyclized-Polyacrylonitrile Modified Carbon Nanofiber Interlayers Enabling Strong Trapping of Polysulfides in Lithium–Sulfur Batteries," *J. Mater. Chem. A*, vol. 4, pp. 12973-12980, 2016.
- [71] F. Wu, W. Li, L. Guan, Y. Ye, J. Qian, X. Yang, Y. Xu and R. Chen "A Polypyrrole-Supported Carbon Paper Acting as a Polysulfide Trap for Lithium–Sulfur Batteries," *RSC Adv.*, vol. 5, pp. 94479-94485, 2015.
- [72] M. Liu, Q. Li, X. Qin, G. Liang, W. Han, D. Zhou, Y. B. He, B. Li, and F. Kang, "Suppressing Self-Discharge and Shuttle Effect of Lithium-Sulfur Batteries with V₂O₅-Decorated Carbon Nanofiber Interlayer," *Small*, Vol. 13, p. 1602539, 2017.
- [73] T. Zhou, W. Lv, J. Li, G. Zhou, Y. Zhao, S. Fan, B. Liu, B. Li, F. Kang and Q. -H Yang, "Twinborn TiO₂–Tin Heterostructures Enabling Smooth Trapping–Diffusion–Conversion of Polysulfides Towards Ultralong Life Lithium–Sulfur Batteries," *Energy Environ. Sci.*, vol. 10, pp. 1694-1703, 2017.
- [74] J. Liu, L. Yuan, K. Yuan, Z. Li, Z. Hao, J. Xiang and Y. Huang, "SnO₂ as a High-Efficiency Polysulfide Trap in Lithium-Sulfur Batteries," *Nanoscale*, vol. 8, pp. 13638-13645, 2016.
- [75] S. Evers and L. F. Nazar, "New Approaches for High Energy Density Lithium-Sulfur Battery Cathodes," *Acc. Chem. Res.*, vol. 46, pp. 1135-1143, 2013.
- [76] A. Manthiram, Y. Fu, S.-H. Chung, C. Zu, and Y.-S. Su, "Rechargeable Lithium-Sulfur Batteries," *Chem. Rev.*, vol. 114, pp. 11751-11787, 2014.
- [77] Y.-X. Yin, S. Xin, Y.-G. Guo, and L.-J. Wan, "Lithium-Sulfur Batteries: Electrochemistry, Materials, and Prospects," *Angew. Chem.*, vol. 52, pp. 13186-13200, 2013.
- [78] R. Chen, T. Zhao, and F. Wu, "From a Historic Review to Horizons Beyond: Lithium-Sulphur Batteries Run on the Wheels," *Chem. Commun.*, vol. 51, pp. 18-33, 2015.
- [79] K. Amine, R. Kanno, and Y. Tzeng, "Rechargeable Lithium Batteries and Beyond: Progress, Challenges, and Future Directions," *MRS Bulletin*, vol. 39, pp. 395-401, 2014.
- [80] S. Waluś, C. Barchasz, R. Bouchet, J.-C. Leprêtre, J.-F. Colin, J.-F. Martin, E. Elkaïm and C. Baetz, "Lithium/Sulfur Batteries Upon Cycling: Structural Modifications and Species Quantification by In Situ and Operando X-Ray Diffraction Spectroscopy," *Adv. Energy Mater.*, vol. 5, p.1500165, 2015.

- [81] M. Cuisinier, C. Hart, M. Balasubramanian, A. Garsuch, and L. F. Nazar, "Radical or Not Radical: Revisiting Lithium–Sulfur Electrochemistry in Nonaqueous Electrolytes," *Adv. Energy Mater.*, vol. 5, pp. 1401801, 2015.
- [82] K. H. Wujcik, T. A. Pascal, C. D. Pemmaraju, D. Devaux, W. C. Stolte, N. P. Balsara, D. Prendergast, "Characterization of Polysulfide Radicals Present in an Ether-Based Electrolyte of a Lithium-Sulfur Battery During Initial Discharge Using In Situ X-Ray Absorption Spectroscopy Experiments and First-Principles Calculations," *Adv. Energy Mater.*, vol. 5, pp. 1500285, 2015.
- [83] R. Xu, J. Lu, and K. Amine, "Progress in Mechanistic Understanding and Characterization Techniques of Li-S Batteries," *Adv. Energy Mater.*, vol. 5, pp. 1500408, 2015.
- [84] C. Barchasz, F. Molton, C. Duboc, J.-C. Leprêtre, S. Patoux, and F. Alloin, "Lithium/Sulfur Cell Discharge Mechanism: An Original Approach for Intermediate Species Identification," *Anal. Chem.*, vol. 84, pp. 3973-3980, 2012.
- [85] S. Waluś, C. Barchasz, J.-F. Colin, J.-F. Martin, E. Elkaïm, J.-C. Leprêtre, and F. Alloin, "New Insight into the Working Mechanism of Lithium–Sulfur Batteries: In Situ and Operando X-Ray Diffraction Characterization," *Chem. Commun.*, vol. 49, pp. 7899-7901, 2013.
- [86] M. Cuisinier, P.-E. Cabelguen, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bolin, M. Balasubramanian, and L. F. Nazar, "Sulfur Speciation in Li–S Batteries Determined by Operando X-ray Absorption Spectroscopy," *J. Phys. Chem. Lett.*, vol. 4, pp. 3227-3232, 2013.
- [87] Y. V. Mikhaylik and J. R. Akridge, "Polysulfide Shuttle Study in the Li/S Battery System," *J. Electrochem. Soc.*, vol. 151, pp. A1969-A1976, 2004.
- [88] Y. Diao, K. Xie, S. Xiong, and X. Hong, "Shuttle Phenomenon – the Irreversible Oxidation Mechanism of Sulfur Active Material in Li–S Battery," *Journal of Power Sources*, vol. 235, pp. 181-186, 2013.
- [89] R. Elazari, G. Salitra, Y. Talyosef, J. Grinblat, C. Scordilis-Kelley, A. Xiao, J. Affinitob and D. Aurbach, "Morphological and Structural Studies of Composite Sulfur Electrodes upon Cycling by HRTEM, AFM and Raman Spectroscopy," *J. Electrochem. Soc.*, vol. 157, pp. A1131-A1138, 2010.
- [90] S.-E. Cheon, K.-S. Ko, J.-H. Cho, S.-W. Kim, E.-Y. Chin, and H.-T. Kim, "Rechargeable Lithium Sulfur Battery: I. Structural Change of Sulfur Cathode During Discharge and Charge," *Journal of The Electrochemical Society*, vol. 150, pp. A796-A799, 2003.
- [91] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. van Schalkwijk, "Nanostructured Materials for Advanced Energy Conversion and Storage Devices," *Nat. Mater.*, vol. 4, pp. 366-377, 2005.
- [92] J. Lu, Z. Chen, Z. Ma, F. Pan, L. A. Curtiss, and K. Amine, "The Role of Nanotechnology in the Development of Battery Materials for Electric Vehicles," *Nat. Nanotech.*, vol. 11, pp. 1031-1038, 2016.

- [93] Y.-G. Guo, J.-S. Hu, and L.-J. Wan, "Nanostructured Materials for Electrochemical Energy Conversion and Storage Devices," *Adv. Mater.*, vol. 20, pp. 2878-2887, 2008.
- [94] P. G. Bruce, B. Scrosati, and J.-M. Tarascon, "Nanomaterials for Rechargeable Lithium Batteries," *Angew. Chem.*, vol. 47, pp. 2930-2946, 2008.
- [95] A. Manthiram, A. Vadivel Murugan, A. Sarkar, and T. Muraliganth, "Nanostructured Electrode Materials for Electrochemical Energy Storage and Conversion," *Energy Environ. Sci.*, vol. 1, pp. 621-638, 2008.
- [96] N. Mahmood and Y. Hou, "Electrode Nanostructures in Lithium-Based Batteries," *Adv. Sci.*, vol. 1, pp.1400012 , 2014.
- [97] L. Dai, D. W. Chang, J.-B. Baek, and W. Lu, "Carbon Nanomaterials for Advanced Energy Conversion and Storage," *Small*, vol. 8, pp. 1130-1166, 2012.
- [98] Z. Yang, J. Ren, Z. Zhang, X. Chen, G. Guan, L. Qiu, Y. Zhang and H. Peng, "Recent Advancement of Nanostructured Carbon for Energy Applications," *Chem. Rev.*, vol. 115, pp. 5159-5223, 2015.
- [99] L. Borchardt, M. Oschatz, and S. Kaskel, "Carbon Materials for Lithium Sulfur Batteries-Ten Critical Questions," *Chem. Eur. J.*, Vol. 22, pp. 7324-7351, 2016.
- [100] D.-W. Wang, Q. Zeng, G. Zhou, L. Yin, F. Li, H.-M. Cheng, I. R. Gentle and G. Q. Lu, "Carbon–Sulfur Composites for Li–S Batteries: Status and Prospects," *J. Mater. Chem. A*, vol. 1, pp. 9382-9394, 2013.
- [101] X. Ji, K. T. Lee, and L. F. Nazar, "A Highly Ordered Nanostructured Carbon-Sulphur Cathode for Lithium-Sulphur Batteries," *Nat. Mater.*, vol. 8, pp. 500-506, 2009.
- [102] X. Li, Y. Cao, W. Qi, L. V. Saraf, J. Xiao, Z. Nie, J. Mietek, J. -G. Zhang, B. Schwenzer and J. Liu "Optimization of Mesoporous Carbon Structures for Lithium–Sulfur Battery Applications," *J. Mater. Chem.*, vol. 21, pp. 16603-16610, 2011.
- [103] J. r. Schuster, G. He, B. Mandlmeier, T. Yim, K. T. Lee, T. Bein, and L. F. Nazar, "Spherical Ordered Mesoporous Carbon Nanoparticles with High Porosity for Lithium-Sulfur Batteries," *Angew. Chem.*, vol. 124, pp. 3651-3655, 2012.
- [104] C. Liang, N. J. Dudney, and J. Y. Howe, "Hierarchically Structured Sulfur/Carbon Nanocomposite Material for High-Energy Lithium Battery," *Chem. Mater.*, vol. 21, pp. 4724-4730, 2009.
- [105] Z. Li, Y. Jiang, L. Yuan, Z. Yi, C. Wu, Y. Liu, P. Strasser, and Y. Huang, "A Highly Ordered Meso@Microporous Carbon-Supported Sulfur@Smaller Sulfur Core–Shell Structured Cathode for Li–S Batteries," *ACS Nano*, vol. 8, pp. 9295-9303, 2014.
- [106] S. Xin, L. Gu, N.-H. Zhao, Y.-X. Yin, L.-J. Zhou, Y.-G. Guo, and L.-J. Wan, "Smaller Sulfur Molecules Promise Better Lithium-Sulfur Batteries," *J. Am. Chem. Soc.*, vol. 134, pp. 18510-18513, 2012.
- [107] Z. Li, L. Yuan, Z. Yi, Y. Sun, Y. Liu, Y. Jiang, Yue Shen, Y. Xin, Z. Zhang and Y. Huang, "Insight into the Electrode Mechanism in Lithium-Sulfur Batteries with Ordered

- Microporous Carbon Confined Sulfur as the Cathode," *Adv. Energy Mater.*, vol. 4, p. 1301473, 2013.
- [108] N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, and L. A. Archer, "Porous Hollow Carbon@Sulfur Composites for High-Power Lithium-Sulfur Batteries," *Angew. Chem.*, vol. 123, pp. 6026-6030, 2011.
- [109] W. Zhou, X. Xiao, M. Cai, and L. Yang, "Polydopamine-Coated, Nitrogen-Doped, Hollow Carbon-Sulfur Double-Layered Core-Shell Structure for Improving Lithium-Sulfur Batteries," *Nano Lett.*, vol. 14, pp. 5250-5256, 2014.
- [110] A. K. Geim and K. S. Novoselov, "The Rise of Graphene," *Nat. Mater.*, vol. 6, pp. 183-191, 2007.
- [111] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric Field Effect in Atomically Thin Carbon Films," *Science*, vol. 306, pp. 666-669, 2004.
- [112] M. Pumera, "Graphene-Based Nanomaterials For Energy Storage," *Energy Environ. Sci.*, vol. 4, pp. 668-674, 2011.
- [113] H. Kim, H.-D. Lim, J. Kim, and K. Kang, "Graphene for Advanced Li/S And Li/Air Batteries," *J. Mater. Chem. A*, vol. 2, pp. 33-47, 2014.
- [114] R. Raccichini, A. Varzi, S. Passerini, and B. Scrosati, "The Role of Graphene for Electrochemical Energy Storage," *Nat. Mater.*, vol. 14, pp. 271-279, 2014.
- [115] J. Zhu, D. Yang, Z. Yin, Q. Yan, and H. Zhang, "Graphene and Graphene-Based Materials for Energy Storage Applications," *Small*, vol. 10, pp. 3480-3498, 2014.
- [116] H. Sun, G.-L. Xu, Y.-F. Xu, S.-G. Sun, X. Zhang, Y. Qiu, S. Yang, "A Composite Material of Uniformly Dispersed Sulfur on Reduced Graphene Oxide: Aqueous One-Pot Synthesis, Characterization and Excellent Performance as the Cathode in Rechargeable Lithium-Sulfur Batteries," *Nano Res.*, vol. 5, pp. 726-738, 2012.
- [117] H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui and H. Dai, "Graphene-Wrapped Sulfur Particles as a Rechargeable Lithium-Sulfur Battery Cathode Material with High Capacity and Cycling Stability," *Nano Lett.*, vol. 11, pp. 2644-2647, 2011.
- [118] B. Ding, C. Yuan, L. Shen, G. Xu, P. Nie, Q. Lai, and X. Zhang, "Chemically Tailoring the Nanostructure of Graphene Nanosheets to Confine Sulfur for High-Performance Lithium-Sulfur Batteries," *J. Mater. Chem. A*, vol. 1, pp. 1096-1101, 2013.
- [119] M.-S. Park, J.-S. Yu, K. J. Kim, G. Jeong, J.-H. Kim, Y.-N. Jo, U. Hwang, S. Kang, T. Woo and Y.-J. Kim, "One-Step Synthesis of a Sulfur-Impregnated Graphene Cathode for Lithium-Sulfur Batteries," *Phys. Chem. Chem. Phys.*, vol. 14, pp. 6796-6804, 2012.
- [120] F.-F. Zhang, X.-B. Zhang, Y.-H. Dong, and L.-M. Wang, "Facile and Effective Synthesis of Reduced Graphene Oxide Encapsulated Sulfur via Oil/Water System for High Performance Lithium Sulfur Cells," *J. Mater. Chem.*, vol. 22, pp. 11452-11454, 2012.

- [121] M.-Q. Zhao, Q. Zhang, J.-Q. Huang, G.-L. Tian, J.-Q. Nie, H.-J. Peng, and F. Wei., "Unstacked Double-Layer Templated Graphene for High-Rate Lithium-Sulphur Batteries," *Nat. Commun.*, vol. 5, p. 3410, 2014.
- [122] H.-J. Peng, J. Liang, L. Zhu, J.-Q. Huang, X.-B. Cheng, X. Guo, W. Ding, W. Zhu and Q. Zhang, "Catalytic Self-Limited Assembly at Hard Templates: A Mesoscale Approach to Graphene Nanoshells for Lithium-Sulfur Batteries," *ACS Nano*, vol. 8, pp. 11280-11289, 2014.
- [123] M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, and A. J. Hart, "Carbon Nanotubes: Present and Future Commercial Applications," *Science*, vol. 339, pp. 535-539, 2013.
- [124] Y.-S. Su, Y. Fu, and A. Manthiram, "Self-Weaving Sulfur-Carbon Composite Cathodes for High Rate Lithium-Sulfur Batteries," *Phys. Chem. Chem. Phys.*, vol. 14, pp. 14495-14499, 2012.
- [125] G. Zhou, D.-W. Wang, F. Li, P.-X. Hou, L. Yin, C. Liu, G. Q. Lu, I. R. Gentle and H.-M. Chen, "A Flexible Nanostructured Sulphur–Carbon Nanotube Cathode with High Rate Performance for Li-S Batteries," *Energy Environ. Sci.*, vol. 5, pp. 8901-8906, 2012.
- [126] L. Sun, M. Li, Y. Jiang, W. Kong, K. Jiang, J. Wang and S. Fan, "Sulfur Nanocrystals Confined in Carbon Nanotube Network as a Binder-Free Electrode for High-Performance Lithium Sulfur Batteries," *Nano Lett.*, vol. 14, pp. 4044-4049, 2014.
- [127] J.-j. Chen, Q. Zhang, Y.-N. Shi, L.-L. Qin, Y. Cao, M.-S. Zheng and Q. -F. Dong, "A Hierarchical Architecture S/MWCNT Nanomicrosphere with Large Pores for Lithium Sulfur Batteries," *Phys. Chem. Chem. Phys.*, vol. 14, pp. 5376-5382, 2012.
- [128] R. Chen, T. Zhao, J. Lu, F. Wu, L. Li, J. Chen, G. Tan, Y. Ye and K. Amine, "Graphene-Based Three-Dimensional Hierarchical Sandwich-Type Architecture for High-Performance Li/S Batteries," *Nano Lett.*, vol. 13, pp. 4642-4649, 2013.
- [129] M.-Q. Zhao, X.-F. Liu, Q. Zhang, G.-L. Tian, J.-Q. Huang, W. Zhu and F. Wei, "Graphene/Single-Walled Carbon Nanotube Hybrids: One-Step Catalytic Growth and Applications for High-Rate Li-S Batteries," *ACS Nano*, vol. 6, pp. 10759-10769, 2012.
- [130] Y. Zhao, W. Wu, J. Li, Z. Xu, and L. Guan, "Encapsulating MWNTs Into Hollow Porous Carbon Nanotubes: a Tube-In-Tube Carbon Nanostructure for High-Performance Lithium-Sulfur Batteries," *Adv. Mater.*, vol. 26, pp. 5113-5118, 2014.
- [131] J. Song, M. L. Gordin, T. Xu, S. Chen, Z. Yu, H. Sohn, J. Lu, Y. Ren, Y. Duan and D. Wang, "Strong Lithium Polysulfide Chemisorption on Electroactive Sites of Nitrogen-Doped Carbon Composites for High-Performance Lithium-Sulfur Battery Cathodes," *Angew. Chem.*, vol. 54, pp. 4325-4329, 2015.
- [132] B. Wang, Y. Wen, D. Ye, H. Yu, B. Sun, G. Wang, D. Hulicova-Jurcakova and L. Wang, "Dual Protection of Sulfur By Carbon Nanospheres and Graphene Sheets for Lithium-Sulfur Batteries," *Chem. Eur. J.*, vol. 20, pp. 5224-5230, 2014.
- [133] M.-S. Song, S.-C. Han, H.-S. Kim, J.-H. Kim, K.-T. Kim, Y.-M. Kang, H. -J. Ahnb, S. X. Douc and J.-Y. Lee, "Effects of Nanosized Adsorbing Material on Electrochemical

- Properties of Sulfur Cathodes for Li/S Secondary Batteries," *J. Electrochem. Soc.*, vol. 151, pp. A791-A795, 2004.
- [134] Y. G. Zhang, Y. Zhao, A. Yermukhambetova, Z. Bakenov, and P. Chen, "Ternary Sulfur/Polyacrylonitrile/Mg_{0.6}Ni_{0.4}O Composite Cathodes for High Performance Lithium/Sulfur Batteries," *J. Mater. Chem. A*, vol. 1, pp. 295-301, 2013.
- [135] X. Ji, S. Evers, R. Black, and L. F. Nazar, "Stabilizing Lithium–Sulphur Cathodes using Polysulphide Reservoirs," *Nat. Commun.*, vol. 2, p. 325, 2011.
- [136] S. Evers, T. Yim, and L. F. Nazar, "Understanding the Nature of Absorption/Adsorption in Nanoporous Polysulfide Sorbents for the Li–S Battery," *J. Phys. Chem. C*, vol. 116, pp. 19653-19658, 2012.
- [137] K. T. Lee, R. Black, T. Yim, X. Ji, and L. F. Nazar, "Surface-Initiated Growth of Thin Oxide Coatings for Li–Sulfur Battery Cathodes," *Adv. Energy Mater.*, vol. 2, pp. 1490-1496, 2012.
- [138] H. Kim, J. T. Lee, D. C. Lee, A. Magasinski, W.-I. Cho, and G. Yushin, "Plasma-Enhanced Atomic Layer Deposition of Ultrathin Oxide Coatings for Stabilized Lithium–Sulfur Batteries," *Adv. Energy Mater.*, vol. 3, pp. 1308-1315, 2013.
- [139] Z. Wei Seh, W. Li, J. J. Cha, G. Zheng, Y. Yang, M. T. McDowell, P. Hsu and Y. Cui, "Sulphur-TiO₂ Yolk-Shell Nanoarchitecture with Internal Void Space for Long-Cycle Lithium-Sulphur Batteries," *Nat. Commun.*, vol. 4, p. 1331, 2013.
- [140] Z. Liang, G. Zheng, W. Li, Z. W. Seh, H. Yao, K. Yan, H. Huang, Y. Xia, C. Liang, W. Zhang, and Y. Cui, "Sulfur Cathodes with Hydrogen Reduced Titanium Dioxide Inverse Opal Structure," *ACS Nano*, vol. 8, pp. 5249-5256, 2014.
- [141] X. Tao, J. Wang, Z. Ying, Q. Cai, G. Zheng, Y. Gan, *et al.*, "Strong Sulfur Binding with Conducting Magnéli-Phase TinO_{2n-1} Nanomaterials for Improving Lithium–Sulfur Batteries," *Nano Lett.*, vol. 14, pp. 5288-5294, 2014.
- [142] H. Yao, G. Zheng, P.-C. Hsu, D. Kong, J. J. Cha, W. Li, Z. W. Seh, M. T. McDowell, K. Yan, Z. Liang, V. K. Narasimhan and Y. Cui, "Improving Lithium-Sulphur Batteries through Spatial Control of Sulphur Species Deposition on a Hybrid Electrode Surface," *Nat. Commun.*, vol. 5, p. 3943, 2014.
- [143] F. Wu, J. Chen, R. Chen, S. Wu, L. Li, S. Chen, T. Zhao, "Sulfur/Polythiophene with a Core/Shell Structure: Synthesis and Electrochemical Properties of the Cathode for Rechargeable Lithium Batteries," *J. Phys. Chem. C*, vol. 115, pp. 6057-6063, 2011.
- [144] H. Chen, W. Dong, J. Ge, C. Wang, X. Wu, W. Lu, L. Chen, "Ultrafine Sulfur Nanoparticles in Conducting Polymer Shell as Cathode Materials for High Performance Lithium/Sulfur Batteries," *Scientific Reports*, vol. 3, p. 1910, 2013.
- [145] W. Li, G. Zheng, Y. Yang, Z. W. Seh, N. Liu, and Y. Cui, "High-Performance Hollow Sulfur Nanostructured Battery Cathode through a Scalable, Room Temperature, One-Step, Bottom-Up Approach," *PNAS*, vol. 110, pp. 7148-7153, 2013.

- [146] F. Wu, J. Chen, L. Li, T. Zhao, and R. Chen, "Improvement of Rate and Cycle Performance by Rapid Polyaniline Coating of a MWCNT/Sulfur Cathode," *J. Phys. Chem. C*, vol. 115, pp. 24411-24417, 2011.
- [147] G. Ma, Z. Wen, J. Jin, Y. Lu, K. Rui, X. Wu, M. Wu, J. Zhang, "Enhanced Performance of Lithium Sulfur Battery with Polypyrrole Warped Mesoporous Carbon/Sulfur Composite," *Journal of Power Sources*, vol. 254, pp. 353-359, 2014.
- [148] W. Zhou, Y. Yu, H. Chen, F. J. DiSalvo, and H. D. Abruña, "Yolk-Shell Structure of Polyaniline-Coated Sulfur for Lithium-Sulfur Batteries," *J. Am. Chem. Soc.*, vol. 135, pp. 16736-16743, 2013.
- [149] X. Liang, Y. Liu, Z. Wen, L. Huang, X. Wang, and H. Zhang, "A Nano-Structured and Highly Ordered Polypyrrole-Sulfur Cathode for Lithium-Sulfur Batteries," *Journal of Power Sources*, vol. 196, pp. 6951-6955, 2011.
- [150] Y. Zhang, Z. Bakenov, Y. Zhao, A. Konarov, T. N. L. Doan, M. Malik, T. Paron and P. Chen, "One-Step Synthesis of Branched Sulfur/Polypyrrole Nanocomposite Cathode for Lithium Rechargeable Batteries," *Journal of Power Sources*, vol. 208, pp. 1-8, 2012.
- [151] Y.-S. Su and A. Manthiram, "Lithium-Sulphur Batteries with a Microporous Carbon Paper as a Bifunctional Interlayer," *Nat. Commun.*, vol. 3, p. 1166, 2012.
- [152] S.-H. Chung, P. Han, R. Singhal, V. Kalra, and A. Manthiram, "Electrochemically Stable Rechargeable Lithium-Sulfur Batteries with a Microporous Carbon Nanofiber Filter for Polysulfide," *Adv. Energy Mater.*, Vol. 5, p. 1500738, 2015.
- [153] F. Zeng, Z. Jin, K. Yuan, S. Liu, X. Cheng, A. Wang, W. Wang and Y. Yang, "High Performance Lithium-Sulfur Batteries with a Permselective Sulfonated Acetylene Black Modified Separator," *J. Mater. Chem. A*, vol. 4, pp. 12319-12327, 2016.
- [154] J. H. Kim, J. Seo, J. Choi, D. Shin, M. Carter, Y. Jeon, C. Wang, L. Hu and U. Paik, "Synergistic Ultrathin Functional Polymer-Coated Carbon Nanotube Interlayer for High Performance Lithium-Sulfur Batteries," *ACS Appl. Mater. Interfaces*, vol. 8, pp. 20092-20099, 2016.
- [155] G. Xu, J. Yuan, X. Tao, B. Ding, H. Dou, X. Yan, Y. Xiao and X. Zhang., "Absorption Mechanism of Carbon-Nanotube Paper-Titanium Dioxide as a Multifunctional Barrier Material for Lithium-Sulfur Batteries," *Nano Res.*, pp. 1-9, 2015.
- [156] G. Liang, J. Wu, X. Qin, M. Liu, Q. Li, Y.-B. He, J. Kim, B. Li, and F. Kang , "Ultrafine TiO₂ Decorated Carbon Nanofibers as Multifunctional Interlayer for High-Performance Lithium-Sulfur Battery," *ACS Appl. Mater. Interfaces*, vol. 8, pp. 23105-23113, 2016.
- [157] F. Liu, Q. Xiao, H. B. Wu, F. Sun, X. Liu, F. Li, Z. Le, L. Shen, G. Wang, M. Cai and Y. Lu, "Regenerative Polysulfide-Scavenging Layers Enabling Lithium-Sulfur Batteries with High Energy Density and Prolonged Cycling Life," *ACS Nano*, vol. 11, pp. 2697-2705, 2017.
- [158] M. Yu, A. Wang, F. Tian, H. Song, Y. Wang, C. Li, J. Hongd and G. Shi., "Dual-Protection of a Graphene-Sulfur Composite By a Compact Graphene Skin and an Atomic Layer

- Deposited Oxide Coating for a Lithium-Sulfur Battery," *Nanoscale*, vol. 7, pp. 5292-5298, 2015.
- [159] H. Yao, K. Yan, W. Li, G. Zheng, D. Kong, Z. W. Seh, V. K. Narasimhan, Z. Liang and Y. Cui., "Improved Lithium–Sulfur Batteries with A Conductive Coating on the Separator to Prevent the Accumulation Of Inactive S-Related Species at The Cathode–Separator Interface," *Energy Environ. Sci.*, vol. 7, pp. 3381-3390, 2014.
- [160] J.-Q. Huang, T.-Z. Zhuang, Q. Zhang, H.-J. Peng, C.-M. Chen, and F. Wei, "Permselective Graphene Oxide Membrane for Highly Stable and Anti-Self-Discharge Lithium-Sulfur Batteries," *ACS Nano*, vol. 9, pp. 3002-3011, 2015.
- [161] M. Shaibani, A. Akbari, P. Sheath, C. D. Easton, P. C. Banerjee, K. Konstas, A. Fakhfour, M. Barghamadi, M. M. Musameh, A. S. Best, T. R  ther, P. J. Mahon, M. R. Hill, A. F. Hollenkamp, and M. Majumder "Suppressed Polysulfide Crossover in Li-S Batteries through a High-Flux Graphene Oxide Membrane Supported on a Sulfur Cathode," *ACS Nano*, vol. 10, pp. 7768-7779, 2016.
- [162] S. Bai, X. Liu, K. Zhu, S. Wu, and H. Zhou, "Metal–Organic Framework-Based Separator for Lithium–Sulfur Batteries," *Nat. Energy*, vol. 1, p. 16094, 2016.
- [163] T.-Z. Zhuang, J.-Q. Huang, H.-J. Peng, L.-Y. He, X.-B. Cheng, C.-M. Chen and Q. Zhang, "Rational Integration of Polypropylene/Graphene Oxide/Nafion as Ternary-Layered Separator to Retard the Shuttle of Polysulfides for Lithium-Sulfur Batteries," *Small*, vol. 12, pp. 381-389, 2015.
- [164] G. Ma, Z. Wen, Q. Wang, C. Shen, P. Peng, J. Jin and X. Wu, "Enhanced Performance of Lithium Sulfur Battery with Self-Assembly Polypyrrole Nanotube Film as the Functional Interlayer," *Journal of Power Sources*, vol. 273, pp. 511-516, 2015.
- [165] Y. Liu, K. Ai, and L. Lu, "Polydopamine and Its Derivative Materials: Synthesis and Promising Applications in Energy, Environmental, and Biomedical Fields," *Chem. Rev.*, vol. 114, pp. 5057-5115, 2014.
- [166] G. C. Li, H. K. Jing, Z. Su, C. Lai, L. Chen, C. C. Yuan, H. H. Li and L. Liu, "A Hydrophilic Separator for High Performance Lithium Sulfur Batteries," *J. Mater. Chem. A*, vol. 3, pp. 11014-11020, 2015.
- [167] F. Wu, Y. Ye, R. Chen, J. Qian, T. Zhao, L. Li and W. Li, "Systematic Effect for an Ultralong Cycle Lithium-Sulfur Battery," *Nano Lett.*, vol. 15, pp. 7431-7439, 2015.
- [168] B. E. Warren, *X-ray Diffraction*: Dover Publications, 1969.
- [169] E. Smith and G. Dent, *Modern Raman Spectroscopy: A Practical Approach*: Wiley, 2005.
- [170] P. Gabbott, *Principles and Applications of Thermal Analysis*: Blackwell Pub., 2008.
- [171] P. J. Goodhew, *Electron Microscopy and Analysis*: Wykeham Publications, 1975.
- [172] J. F. Watts and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*: Wiley, 2003.

- [173] J. Rouquerol, F. Rouquerol, and K. S. W. Sing, *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*: Elsevier Science, 1998.
- [174] A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*: Wiley, 2000.
- [175] R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, "Carbon Nanotubes--The Route Toward Applications," *Science*, vol. 297, pp. 787-792, 2002.
- [176] A. T. Ward, "Raman Spectroscopy of Sulfur, Sulfur-Selenium, and Sulfur-Arsenic Mixtures," *J.Phys. Chem.*, vol. 72, pp. 4133-4139, 1968.
- [177] X. Gu, C.-j. Tong, B. Wen, L.-m. Liu, C. Lai, and S. Zhang, "Ball-Milling Synthesis of ZnO@Sulphur/Carbon Nanotubes and Ni(OH)₂@Sulphur/Carbon Nanotubes Composites for High-Performance Lithium-Sulphur Batteries," *Electrochimica Acta*, vol. 196, pp. 369-376, 2016.
- [178] F. Zhang and L. Qi, "Recent Progress in Self-Supported Metal Oxide Nanoarray Electrodes for Advanced Lithium-Ion Batteries," *Adv. Sci.*, vol. 3, p. 1600049, 2016.
- [179] J. Liu, J. She, S. Deng, J. Chen, and N. Xu, "Ultrathin Seed-Layer for Tuning Density of ZnO Nanowire Arrays and Their Field Emission Characteristics," *J.Phys. Chem. C*, vol. 112, pp. 11685-11690, 2008.
- [180] T. Ma, M. Guo, M. Zhang, Y. Zhang, and X. Wang, "Density-Controlled Hydrothermal Growth of Well-Aligned ZnO Nanorod Arrays," *Nanotechnology*, vol. 18, p. 035605, 2007.
- [181] L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai and P. Yang, "General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds," *Nano Lett.*, vol. 5, pp. 1231-1236, 2005.
- [182] S. Xu and Z. L. Wang, "One-Dimensional ZnO Nanostructures: Solution Growth and Functional Properties," *Nano Res.*, vol. 4, pp. 1013-1098, 2011.
- [183] M. Inagaki, Y. Yang, and F. Kang, "Carbon Nanofibers Prepared via Electrospinning.," *Adv. Mater.*, vol. 24, pp. 2547-2566, 2012.
- [184] G. Babu, K. Ababtain, K. Y. S. Ng, and L. M. R. Arava, "Electrocatalysis of Lithium Polysulfides: Current Collectors as Electrodes in Li/S Battery Configuration," *Sci. Rep.*, vol. 5, p. 8763, 2015.
- [185] Q. Zhang, Y. Wang, Z. W. Seh, Z. Fu, R. Zhang, and Y. Cui, "Understanding the Anchoring Effect of Two-Dimensional Layered Materials for Lithium–Sulfur Batteries," *Nano Lett.*, vol. 15, pp. 3780-3786, 2015.
- [186] D. Li and Y. Xia, "Fabrication of Titania Nanofibers by Electrospinning," *Nano Lett.*, vol. 3, pp. 555-560, 2003.
- [187] Y. Ye, F. Wu, Y. Liu, T. Zhao, J. Qian, Y. Xing W.Li, J. Huang, L. Li, Q. Huang, X. Bai and R. Chen, "Toward Practical High-Energy Batteries: A Modular-Assembled Oval-Like Carbon Microstructure for Thick Sulfur Electrodes," *Adv. Mater.*, 2017.