DEVELOPMENT AND FABRICATION OF PROTEINS AS MULTIFUNCTIONAL MATERIALS FOR ENERGY STORAGE APPLICATIONS

By

XUEWEI FU

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY
Materials Science and Engineering Program

JULY 2019

© Copyright by XUEWEI FU, 2019
All Rights Reserved
To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of XUEWEI FU find it satisfactory and recommend that it be accepted.

______________________________
Weihong (Katie) Zhong, Ph.D., Chair

______________________________
Louis Scudiero, Ph.D., Co-Chair

______________________________
Jin Liu, Ph.D.
ACKNOWLEDGMENT

First of all, I would like to express my deepest gratitude to my advisor, Dr. Weihong (katie) Zhong, for giving me this precious opportunity to conduct research in her lab at the moment I got lost four years ago. Her continuous support on my life and research has helped me overcome the difficult time in Pullman. Her enthusiasm and motivation about research have inspired me to persist in my research. Without her constant encouragement, instructive guidelines and immense knowledge, I would have never made today’s achievements. I could not have imagined having a better advisor and mentor for my Ph.D study.

I would like to give my sincere thanks to my co-advisor, Dr. Louis Scudiero, for his patience, valuable discussions and encouraging comments. I appreciate much the opportunity that Dr. Scudiero offered me for serving as a teaching assistant. It has been a pleasure working with him, and this special experience will help me throughout my life. I would also like to gratefully thank the other committee member, Dr. Jin Liu, for his professional and religious attitude toward research and helpful advices for my research. The collaboration with him has helped me improve the writing skills and critical thinking capability.

My special thanks go to Dr. Yu (Will) Wang who has selflessly helped me a lot in three years. He has been always strict with me, making me grow up quickly. His excellent creativity, vast knowledge and crucial insight have led my way to the world of research. Without his patience, kindness and efforts, I would have never performed my research so productively. Without continuous discussions and guidance from him, I would have never gained much understanding and knowledge about battery materials.

I wish to thank all my group members: Dr. Tian Liu, Dr. Hamid Souzandeh, Mr. Allen Eyler, Ms. Lu Chen, Mr. Xiaolin Wang, Dr. Yun Huang, Dr. Yichao Li, Dr. Jing Wang, Dr.
Huafeng Tian, Dr. Xin Fan, Dr. Lushi Kong, Ms. Min Chen, Mr. Juejing Liu and Mr. Chenfeng Ding. I greatly appreciate their continuous support and inspiring discussions. I would like to specially thank Mr. Xiaolin Wang and Ms. Lu Chen for their kind help in the first year here, which eased my anxiety. The friendship with all of them is priceless and has made me live through the hard time.

Finally, I would like to thank my beloved parents and little brother who have always supported me whatever decisions I make and given their endless love to me. I am so grateful to my grandmother who passed away last year. She raised me up and took care of me carefully. Having no chance to repay her is a regret for me forever. I would like to say: Thank you so much for everything you did for me and I love you as always!

The financial support from USDA NIFA 2015-67021-22911 and NSF CMMI 1463616 is also greatly acknowledged.
Abstract

by Xuewei Fu, Ph.D.
Washington State University
July 2019

Chair: Weihong (Katie) Zhong

Safe and high-energy batteries are the ultimate goal of development trends for advanced energy storage devices. Realization of this goal demands for developing (i) high-performance solid electrolytes for substituting today’s flammable liquid electrolytes, and (ii) high-capacity electrodes capable of storing more energy than current electrodes. In this dissertation, proteins have been exploited for achieving above two objectives.

This dissertation includes four parts. The first part Introduction describes the overview of lithium-based batteries and the development trends. The second part including Chapters 2, 3 and 4, provide studies on utilizing protein for advanced solid polymer electrolytes (SPEs). In Chapter 2, a novel protein-based solid electrolyte is fabricated, and the unique ion-conduction mechanism is analyzed. Different from conventional SPEs, the protein-based solid electrolyte reveals a unique decoupled ion-conduction mechanism. In Chapters 3 and 4, composite electrolytes enhanced by protein/TiO₂ hybrid nanofillers are studied. Two types of hybrid nanofillers are fabricated:
protein/TiO₂ nanoparticles (Chapter 3) and protein/TiO₂ nanowires (Chapter 4). Chapter 3 mainly discusses the proper way for manipulating protein configuration by TiO₂ nanoparticles and concludes that a favorable protein configuration benefits transport of lithium ions. Chapter 4 outlines the study of core-shell protein/TiO₂ nanowires for further improving the electrolyte properties. Adding these two hybrid nanofillers into polyethylene oxide (PEO) electrolytes, the physicochemical, mechanical and electrochemical properties are improved. Protein/TiO₂ nanowire system shows further improvement compared with the nanoparticle counterpart. In the third part (Chapter 5 and 6), to address the critical issues of high-capacity sulfur cathodes, proteins are adopted for binder materials and battery interlayers. In Chapter 5, a protein-based binder with abilities of buffering large volume change of sulfur, adsorbing polysulfides and promoting electrochemical reactions is studied. These advantages warrant high loading sulfur cathodes and excellent battery performance. In Chapter 6, a unique interlayer (protein nanofilter) is fabricated, and the rational porous structure and surface properties of the nanofilter enable strong binding with polysulfides. Consequently, the electrochemical performance of the Li-S batteries is enhanced. In the last part, Chapter 7, the critical conclusions drawn from the studies are summarized and the outlook is proposed.
TABLE OF CONTENTS

ACKNOWLEDGMENT ........................................................................................................ iii

ABSTRACT .............................................................................................................................. v

LIST OF TABLES ................................................................................................................... xii

LIST OF FIGURES .................................................................................................................. xiii

CHAPTER 1 BACKGROUND AND OBJECTIVE .................................................................. 1

1.1 Lithium-ion batteries (LIBs) .......................................................................................... 1
  1.1.1 Configuration and working mechanism ................................................................. 1
  1.1.2 Key performance factors ....................................................................................... 3

1.2 Development trends for advanced batteries ................................................................. 4
  1.2.1 Pursuit of safety ........................................................................................................ 4
  1.2.2 Pursuit of capacity: beyond “LIBs” ......................................................................... 6
  1.2.3 Solution to improving safety: solid-state LIBs ....................................................... 8
  1.2.4 Solution to improving capacity: lithium-sulfur (Li-S) battery .............................. 10

1.3 Overview of electrolytes of LIBs .................................................................................. 12
  1.3.1 Liquid electrolytes ................................................................................................. 12
  1.3.2 Solid electrolytes ................................................................................................... 15
  1.3.3 Gel polymer electrolytes ....................................................................................... 18
  1.3.4 Advantages and disadvantages of various electrolytes .......................................... 19

1.4 Solid polymer electrolytes (SPEs) for LIBs ................................................................. 20
  1.4.1 Structures of SPEs ................................................................................................. 20
  1.4.2 Strategies for improving SPE performance ......................................................... 21
  1.4.3 Bio-based SPEs ..................................................................................................... 23
  1.4.4 Critical challenge: trade-off between ionic conductivity and mechanical properties . 25
1.5 High-energy batteries: Li-S batteries ................................................................. 26
  1.5.1 Critical challenges for Li-S batteries .............................................................. 26
  1.5.2 Binder materials for improving performance of Li-S batteries ....................... 28
  1.5.3 Interlayers for improving performance of Li-S batteries ............................... 30
1.6 Protein for energy storage .................................................................................. 33
1.7 Problem statement and research objectives ....................................................... 35
  1.7.1 Problem statement ......................................................................................... 35
  1.7.2 Research objectives ....................................................................................... 37
1.8 Dissertation structure ......................................................................................... 39

CHAPTER 2 PROTEIN-BASED SOLID ELECTROLYTS WITH DECOUPLED ION-TRANSPORT ................................................................. 41
  2.1 Introduction ....................................................................................................... 41
  2.2 Experimental ..................................................................................................... 42
    2.2.1 Electrolyte preparation ................................................................................. 42
    2.2.2 Molecular simulations ............................................................................... 43
    2.2.2 Characterization ......................................................................................... 44
  2.3 Results and discussion ...................................................................................... 46
    2.3.1 Protein denaturation and solubility for lithium salt .................................... 46
    2.3.2 Electrochemical and mechanical properties ................................................. 49
    2.3.3 Mechanism studies ..................................................................................... 55
  2.4 Conclusions ...................................................................................................... 64

CHAPTER 3 COMPOSITE ELECTROLYTES WITH FAST ION-CONDUCTION BY MANIPULATING PROTEIN CONFIGURATION ................................................. 65
  3.1 Introduction ....................................................................................................... 65
  3.2 Experimental ..................................................................................................... 68
CHAPTER 6 PROTEIN NANOFILTER FOR TRAPPING POLYSULFIDES AND PROMOTING LI⁺-TRANSPORT IN LI-S BATTERIES .......................................................... 151

6.1 Introduction .......................................................................................................................... 151

6.2 Experimental .......................................................................................................................... 153

6.2.1 Sample preparation ............................................................................................................. 153

6.2.2 Characterization .................................................................................................................. 155

6.2.3. Simulation studies ............................................................................................................ 156

6.3 Results and discussion ........................................................................................................... 159

6.3.1 Design strategy .................................................................................................................. 159

6.3.2 Fabrication studies ............................................................................................................. 161

6.3.3 PSNF properties ................................................................................................................. 165

6.4 Conclusions .......................................................................................................................... 179

CHAPTER 7 SUMMARY OF CONCLUSIONS AND OUTLOOK .............................................. 180

7.1 Summary of conclusions ........................................................................................................ 180

7.1.1 Protein-based solid electrolytes ........................................................................................ 180

7.1.2 Protein/TiO₂ hybrid nanofillers for composite electrolytes ................................................ 181

7.1.3 Protein-based binder for Li-S batteries ............................................................................. 182

7.1.4 Protein nanofilter for Li-S batteries ................................................................................... 183

7.2 Outlook .................................................................................................................................. 184

REFERENCES ............................................................................................................................. 186
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Comparison of different types of ionic liquid electrolytes</td>
<td>14</td>
</tr>
<tr>
<td>1.2</td>
<td>Comparison of important properties of various types of electrolytes for LIBs</td>
<td>19</td>
</tr>
<tr>
<td>1.3</td>
<td>State-of-the-art bio-based solid electrolytes</td>
<td>24</td>
</tr>
<tr>
<td>2.1</td>
<td>Amino acid profile of soy protein</td>
<td>46</td>
</tr>
<tr>
<td>6.1</td>
<td>Physical properties of various CB-based nanocomposite coating</td>
<td>162</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>(a) Comparison of various energy storage devices with respect to energy/power densities. (b) Illustration of typical configurations of a lithium-ion battery. (c) Common materials for primary components of lithium-ion batteries.</td>
</tr>
<tr>
<td>1.2</td>
<td>Plots showing the discharge potential (vs. Li/Li⁺) versus specific capacity of (a) common intercalation-type cathode materials (experimental), (b) conversion-type cathode materials (theoretical), (c) conversion-type anode materials (experimental) and (d) overview of average discharge potential of various types of electrode materials.</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematic illustration of (a) intercalation reaction-based LIBs and (b) conversion reaction-based Li-S batteries.</td>
</tr>
<tr>
<td>1.4</td>
<td>Voltage profile of a Li–S battery indicating the phase-transformation of polysulfides. (b) Electrochemical reactions of sulfur-related species with Li and the corresponding reaction potential.</td>
</tr>
<tr>
<td>1.5</td>
<td>Mechanisms of ion transport for SPEs via intrachain/interchain ion or ion cluster hopping.</td>
</tr>
<tr>
<td>1.6</td>
<td>The distribution of Li ions in SPEs in different states: (a) in amorphous state, (b) in crystalline state and (c) around nanoparticle interphases.</td>
</tr>
<tr>
<td>1.7</td>
<td>Schematic illustration of shuttle effect mechanism in Li-S batteries based on liquid electrolytes.</td>
</tr>
<tr>
<td>1.8</td>
<td>Schematic illustration of the microstructure changes of sulfur cathodes with a multifunctional robust binder as compared with a traditional binder.</td>
</tr>
<tr>
<td>1.9</td>
<td>Schematic illustration of Li-S batteries with (a) a conventional separator and (b) an interlayer inserted between the sulfur cathode and separator.</td>
</tr>
<tr>
<td>1.10</td>
<td>Four-level structures of proteins: primary, secondary, tertiary and quaternary structures.</td>
</tr>
<tr>
<td>1.11</td>
<td>Research objectives and specific tasks for achieving the targeted properties via fabricating two types of SPEs: bio-based SPEs and bio-filler enhanced SPEs.</td>
</tr>
<tr>
<td>1.12</td>
<td>Schematic of the dissertation structure.</td>
</tr>
<tr>
<td>2.1</td>
<td>Fabrication process of protein-based solid electrolytes with controlling the loading of lithium salt and evaporation temperature for removing the solvents.</td>
</tr>
<tr>
<td>2.2</td>
<td>Morphology and particle size distribution of original and denatured SP.</td>
</tr>
</tbody>
</table>
Figure 2.3. Solubility of LiClO₄ in SP at room temperature......................................................... 48

Figure 2.4. Ion-conductivity of SP solid electrolytes with different loading of lithium salt prepared at different evaporation temperatures ................................................................. 49

Figure 2.5. Ionic conductivity of protein-based solid electrolyte at room temperature............. 51

Figure 2.6. Electrochemical and mechanical properties of the SP solid electrolyte prepared with 30 wt% of LiClO₄ loading ....................................................................................... 53

Figure 2.7. (a) Crystal structure of the 7S homotrimer formed by three α' subunits. The purple portion representing the whole 7S is simulated in our simulations. (b) Simulation box of acetic acid-water solution containing SPI (purple), acetic acid molecules (green) and water molecules (red)........................................................................................................ 55

Figure 2.8. Molecular simulations of denaturation of the soy protein.................................... 56

Figure 2.9. Molecular simulations of protein-ion interactions. .................................................. 57

Figure 2.10. Morphological studies of SP solid electrolytes with an evaporation temperature of 25 °C with varying LiClO₄ loadings ................................................................................. 59

Figure 2.11. Morphological studies of SP solid electrolytes with an evaporation temperature of 40 °C with varying LiClO₄ loadings ............................................................................... 60

Figure 2.12. Decoupled ion transport mechanism ...................................................................... 63

Figure 3.1. Schematic for the preparation of TiO₂-soy protein hybrid nanofillers with different protein configuration and ion-conductive properties ....................................................... 72

Figure 3.2. Morphology studies of the TiO₂ nanoparticles, TiO₂-SP hybrids and the resultant composite polymer electrolytes (CPEs) .................................................................................. 74

Figure 3.3. TGA curves of TiO₂-(SP-open) hybrid nanofiller compared with untreated TiO₂... 76

Figure 3.4. (a) Comparison of room temperature ionic conductivity for pure PEO-LiClO₄ electrolyte, CPEs with 5 wt% loadings of various nanofillers. (b) Ionic conductivity of CPEs with the two types of hybrid nanofillers at varying loadings (weight ratio of TiO₂ : SP = 4:1) ........... 77

Figure 3.5. Morphological studies of CPEs with vary loadings of TiO₂-(SP-open) hybrid ....... 78

Figure 3.6. Ionic conductivity and mechanical properties of optimized CPEs ....................... 80

Figure 3.7. (a) Storage modulus of pure PEO-LiClO₄ electrolyte and CPEs with 5 wt% loading various nanofillers. (b) Summary of ionic conductivity and mechanical properties of the CPEs 81

Figure 3.8. Electrochemical properties and battery performance of CPEs ............................ 83
Figure 3.9. Adhesion properties studies of the CPEs with TiO$_2$-SP hybrid nanofillers. .............. 84

Figure 3.10. Molecular simulation studies of the soy-protein (SP) denaturation with or without TiO$_2$. ................................................................................................................................. 87

Figure 3.11. Simulation studies on the interactions between denatured SP and TiO$_2$ nanoparticles. ......................................................................................................................................... 90

Figure 4.1. Fabrication of core-shell protein@TiO$_2$ NWs......................................................... 100

Figure 4.2. FTIR spectra and EDS mapping of TiO$_2$ NWs. ......................................................... 101

Figure 4.3. SEM, TEM images and EDS mapping of TiO$_2$ NWs and core-shell SP@TiO$_2$ NWs.. ........................................................................................................................................... 102

Figure 4.4. XRD patterns and FTIR spectra of SP, TiO$_2$ NWs and SP@TiO$_2$ NWs.............. 103

Figure 4.5. (a) SEM images of CPEs with 10 wt% loading of various nanofillers. (b) Differential scanning calorimetry (DSC) curves of various CPEs loaded with 10 wt% nanofillers compared with pure PEO and PEO electrolyte........................................................................................................... 105

Figure 4.6. Ionic conductivity of CPEs with 10 wt% loading of various nanofillers................. 106

Figure 4.7. Mechanical properties of CPEs with various nanofillers.. ........................................ 109

Figure 4.8. Electrochemical properties of CPEs with various nanofillers. sference number of CPEs compared with pure PEO electrolyte................................................................. 110

Figure 4.9. The role of protein in dissociating lithium salts and promoting ion-conduction. .... 113

Figure 4.10. Electrochiemical properteis of CPEs................................................................. 115

Figure 4.11. Battery performance of CPEs.................................................................................. 117

Figure 5.1. Schematic illustration of the design strategy of the robust and multi-functional binder ........................................................................................................................................ 128

Figure 5.2. Properties of SP-PAA binder.................................................................................. 130

Figure 5.3. Microstructures of S cathodes with different binders.............................................. 132

Figure 5.4. Mechanical properties of dry S cathodes.............................................................. 134

Figure 5.5. Mechanical properties of wet S cathodes.............................................................. 136

Figure 5.6. Peel-off testing and electrical conductivity measurement of S cathodes .......... 138

Figure 5.7. Electrochemical performance of the batteries with different S cathodes.......... 142
Figure 5.8. (a) Open-circuit voltage (OCV) of S cathodes with different binders. (b) Photographs showing various composites of binder/CB in Li$_2$S$_6$ solution. ................................................................. 144

Figure 5.9. DFT calculations of various binders for binding polysulfides ........................................... 147

Figure 5.10. Voltage profiles of S cathodes with 2.8 mg/cm$^2$ S loading.............................. 148

Figure 5.11. Electrochemical performance of Li-S batteries with high S loading. .................... 149

Figure 6.1. Molecular structure of Li$_2$S$_4$ at stable state ................................................................. 157

Figure 6.2. Design and fabrication of polysulfides nano-filter (PSNF) based on self-assembled protein@CB nanocomposite................................................................. 160

Figure 6.3. Wetting behavior of PVDF/CB dispersion on separator and microstructure of PVDF/CB coating.............................................................................................................. 161

Figure 6.4. Fabrication studies of gelatin/CB by deionized (DI) water........................................... 163

Figure 6.5. Fabrication studies of gelatin/CB (PSNF) by mixture solvent of acetic acid (AA) and DI water (AA/DI)......................................................................................................................... 164

Figure 6.6. Compression stress versus indentation time for PSNF as compared with PVDF-CB50% ................................................................................................................................. 166

Figure 6.7. Polysulfides filtration studies by diffusion testing and molecular simulation studies. ......................................................................................................................................................................................... 167

Figure 6.8. Unit structure of gelatin ........................................................................................................ 168

Figure 6.9. Charge/discharge profiles of Li-S batteries with PSNF-coated Celgard separator as compared with control systems................................................................................................................................. 170

Figure 6.10. Rate capability, cycle stability and impedance studies of the PSNF-coating as compared with other separator coatings. .......................................................................................... 174

Figure 6.11. (a) cycle performance comparison at a current density of 0.3 A/g. (b) – (c) SEM images of PSNF before and after 200 cycles of charging/discharging, respectively................. 175

Figure 6.12. Air and ions flow resistance studies of separator coatings ........................................... 177
CHAPTER 1
BACKGROUND AND OBJECTIVE

1.1 Lithium-ion batteries (LIBs)

1.1.1 Configuration and working mechanism

Figure 1.1. (a) Comparison of various energy storage devices with respect to energy/power densities. (b) Illustration of typical configurations of a lithium-ion battery. (c) Common materials for primary components of lithium-ion batteries.

Rapid development of portable electronics, electric vehicles and stationary storage systems calls for urgent demands for next-generation energy storage devices (ESDs) and new energy
Figure 1.1 (a) compares several categories of ESDs in terms of two critical parameters: energy density and power density. Energy density refers to the amount of energy that can be stored, while power density indicates how fast the energy can be extracted out. This comparison clearly suggests that among the various ESDs, lithium-ion batteries (LIBs) present high performances in energy/power densities, making them promising and advanced ESDs.\textsuperscript{1–3} LIBs are typically composed of two electrodes, including a cathode and an anode, coated on highly electrical-conductive metal substrates as current collectors. The two electrodes are connected by a separator/electrolyte, which are electronically insulated by the separator and ionically conductive by the electrolyte. According to the cell configuration shown in Figure 1.1 (b), one can see that the working mechanism of LIBs relies on electrochemical reactions between the two electrodes, including intercalation, conversion and alloying with Li ions.\textsuperscript{4} Specifically, in charging state, Li ions are emitted from the cathode, transported via an electrolyte and finally stored in the anode. In discharging state, on the contrary, Li ions diffuse from the anode to the cathode.

Figure 1.1 (c) shows the materials for the primary components of LIBs. The first priority requirement for electrode materials is warranting reversible doping/de-doping of Li ions in charging/discharging processes. Thus far, a vast variety of electrode materials have been exploited. Li-containing compounds (e.g. LiCoO\textsubscript{2}, LiFePO\textsubscript{4}, LiMN\textsubscript{2}O\textsubscript{4}, etc.)\textsuperscript{5} that are the most popular category and transition metal oxides (V\textsubscript{2}O\textsubscript{5}\textsuperscript{6,7}, etc.) are intensively studied for cathode materials; meanwhile, graphite\textsuperscript{8,9}, hard carbon\textsuperscript{10,11}, transition metal oxides (Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{12,13}, CuO\textsuperscript{14,15}, etc.) and silicon\textsuperscript{16,17} are the primary anode materials. Electrolyte is the only medium that connects all the components and plays a vital role in controlling the dynamics of Li ions inside of the battery. Electrolyte is usually a liquid solution with dissolved Li salts. The solvated Li ions are able to diffuse through this medium between the two electrodes. Solid electrolytes are another type of ion...
conductor applicable in LIBs, which will be discussed in detail in Section 1.3.2. In addition, to ensure fast transport of Li ions, the separator is typically a porous insulative membrane made of plastics (e.g. polyethylene, polypropylene) or nonwovens.\textsuperscript{[18,19]}

1.1.2 Key performance factors

LIB is a device converting chemical energy to electric energy by electrochemical reactions. The reversible electrochemical reactions lead to the migration of Li ions and generate electric currents. To evaluate a battery for practical use, several key parameters are taken into consideration:

(1) Voltage (potential): The voltage of the battery is determined by the difference of the chemical potential between the cathode ($\mu_c$) and anode ($\mu_a$) determined by the free energy of the electrochemical reaction, which is also known as open circuit voltage ($V_{OC}$)\textsuperscript{[20]}:

$$V_{oc} = \frac{\mu_a - \mu_c}{e}$$ (eqn. 1.1)

where $e$ refers to the magnitude of the electronic charge. It is noted that the voltage is also limited by the electrochemical stability window of the electrolytes.

(2) Theoretical capacity: The theoretical capacity ($Q$) of the electrodes is an inherent property. It is determined by the number of electrons that can be transferred during the electrochemical reactions and the molecular weight of the electrode materials:

$$Q = \frac{nF}{M}$$ (eqn. 1.2)

where $n$, $F$ and $M$ refer to the number of electrons, Faraday constant and molecular weight of electrode materials, respectively.
(3) Energy density: The energy density \(E\) indicates the capacity of the battery to store energy. It is an essential parameter for practical performance and is related to both voltage and capacity:

\[
E = \frac{QV}{m}
\]  
(eqn. 1.3)

where \(Q\), \(V\) and \(m\) refer to the capacity, voltage and mass of the battery, respectively.

(4) Power density: The power density \(P\) reflects the ability to deliver the energy:

\[
P = \frac{UI}{m}
\]  
(eqn. 1.4)

where \(U\), \(I\) and \(m\) refer to voltage, current and mass of the battery, respectively.

1.2 Development trends for advanced batteries

The pursuit for next-generation batteries has driven the evolution of battery components and innovative battery technologies. Advanced batteries should satisfy two important requirements: high safety and energy density. In current stage, simultaneously achieving these two targets can be extremely difficult, limited by the electrochemistry and battery fabrication technologies. Therefore, research efforts have focused on developing advanced batteries with emphasis on either aspect.

1.2.1 Pursuit of safety

The gradual popularization of electric vehicles and personal electronics has brought about increasing demands for highly-safe ESDs, which is even more critical for highly-demanding application environments such as aero crafts. As is well known that, liquid electrolytes are still dominating the battery community at present. In fact, batteries are vulnerable to thermal runaway (e.g. by internal short circuit, separator defects or misuse), which may eventually result in
combustion due to the flammable organic liquid electrolytes.\[^{[21]}\] For example, the grounding of Boeing 787 in 2013 and explosion of Samsung Note 7 recently were both caused by battery overheating and combustion. For improving the energy density while keeping mature electrode materials, people are putting many efforts to increase electrochemical reaction efficiency and decrease the component percentage of inert materials. Because the primary materials that generate energy are electrodes, reducing the thickness of inert separators is believed to be effective to improve energy/power densities.\[^{[22]}\] However, this action poses safety concerns, as the thinner separator increases short-circuit risks. It is therefore anticipated that more critical efforts are needed to fabricate perfectly safe LIBs via either reforming the battery fabrication/protection technologies or totally replacing the threatening components such as organic liquid electrolytes. In such a context, solid-state LIBs are of great interest and represent an attractive solution, which resolve the safety issues from the root. Moreover, solid-state LIBs exhibit many advantages in addition to good safety that will be discussed in detail in following sections.
Figure 1.2. Plots showing the discharge potential (vs. Li/Li$^+$) versus specific capacity of (a) common intercalation-type cathode materials (experimental), (b) conversion-type cathode materials (theoretical), (c) conversion-type anode materials (experimental) and (d) overview of average discharge potential of various types of electrode materials.$^{[23]}$

1.2.2. Pursuit of capacity: Beyond “LIBs”

Another category of efforts is to search for new electrode materials being able to offer much higher capacity. This strategy compared with reducing inert material percentage, can maintain most of current battery technologies and relatively high safety. As defined in Section 1.1.2, energy density is proportional to the capacity and voltage. This principle indicates that higher capacity and voltage significantly promote the energy density of the batteries. Today’s LIBs that use Li-containing compounds as the electrodes have almost reached their theoretical energy
limits. The exploration of innovative electrodes and battery systems is thus encouraged. Rechargeable Li batteries directly using Li metal as the anode have emerged as a type of appealing battery system, which are also known as “beyond LIBs”. It is noted that Li metal when used as an anode, exhibits remarkable advantages of ultrahigh theoretical capacity (3860 mAh/g), the lowest redox potential (-3.04 V vs. the standard hydrogen electrode) and low bulk density (0.53 g/cm³)[24].

Figure 1.2 compares several classes of electrode materials in terms of the specific capacity and voltage (potential) vs. Li/Li⁺ for Li-based batteries including both LIBs and Li metal batteries. As shown in Figure 1.2 (a) and (b), as compared with the traditional intercalation-type cathodes, conversion-type cathodes deliver substantially higher specific capacities, which is especially true for the sulfur cathode. Similarly, as shown in Figure 1.2 (c) and (d) conversion-type anode materials such as silicon and phosphate show remarkable specific capacity in comparison of graphite (theoretical specific capacity: 372 mAh/g[25]). However, these high-performance electrode materials usually suffer from dissolution of active materials in liquid electrolytes or large volume change in electrochemical reactions, which remain critical obstacles preventing them from broad practical applications.

The discussion above suggests two important development trends for advanced rechargeable Li-based batteries: (1) improve the battery safety; (2) improve the electrode capacity. Eventually, the two directions would converge into one ultimate target leading to safe and high-energy Li-based batteries. The following sections will discuss separately the strategies and critical challenges for the two trends.
1.2.3 Solution to improving safety: solid-state LIBs

1.2.3.1 Solid-state LIBs

Solid-state LIBs use solid ion conductors as the ion-conduction media, different from the conventional LIBs with liquid electrolytes. Accompanied with the liquid-based LIBs is the safety issues. The electrodes of LIBs consist of solid particles (e.g. active materials, conductive fillers) glued together by a polymer binder. To ensure good interfacial contacts among electrode/electrolyte/separator, a huge compression force is applied inside the battery system. The rigid bulk properties and uneven surfaces of electrodes make the battery vulnerable to internal short circuit, especially with a thin separator. The generated “hot spot” results in the local meltdown of the separator, which greatly increases the battery temperature and eventually drives thermal runaway and even serious combustion. The main reason for the battery combustion is the flammable and volatile organic liquid electrolytes that are commercially used in current LIBs. Therefore, to improve the battery safety, removing the primary hazards (e.g. organic liquid electrolytes) from the root is an attractive solution.

In contrast to liquid electrolyte-based LIBs, solid-state LIBs use solid electrolytes as the ion-conducting media. Compared with the LIBs with liquid electrolytes, solid-state LIBs have advantages in four aspects:

(1) Safety: As introduced above, the safety issues of batteries are primarily caused by combustion of liquid electrolytes under the circumstance of overheating. Solid-state LIBs replace the use of flammable and volatile liquid electrolytes by solid electrolytes that are nonflammable. This effectively eliminates the risks of combustion or explosion by liquid electrolytes.
(2) Life span: The degradation and decomposition of liquid electrolytes under specific conditions is one of the reasons for battery performance decay. Solid electrolytes present better chemical/thermal/electrochemical stabilities as compared with liquid electrolytes. These merits warrant the long-term stability of the solid electrolytes and thereof improve the life span of the LIBs.

(3) Packing volume: Reducing the packing volume can enhance the energy density, which enables to encase more active materials in a certain volume. As is well known that, the conventional separators used in liquid electrolyte-based LIBs are in the range of 20 ~ 30 µm\(^{19}\). A solid electrolyte serving as both a separator and an ion conductor removes the use of conventional separators. More importantly, the solid-state technology can decrease the thickness of solid electrolytes down to 3 ~ 4 µm, which effectively saves the packing space.

(4) Design flexibility: The increasing interests of flexible and wearable electronic devices require advanced LIBs with good safety and design flexibility. Solid electrolytes possess good mechanical properties, in contrast to liquid electrolytes having no mechanical strength. In addition, solid-state LIBs show significant advantages in design flexibility. High-elastic-modulus solid electrolytes such as ceramic electrolytes are appropriate for rigid battery design; low-elastic-modulus solid electrolytes such as polymer electrolytes are believed to be suitable candidates for flexible battery design.

1.2.3.2 Critical challenges for solid-state LIBs

Despite that solid-state LIBs show overwhelming advantages in safety, mechanical performance, design flexibility, etc., the practical applications of them are hindered by the limited performance of solid electrolytes. The main challenges are the low ionic conductivity and poor
interfacial properties. The ionic conductivity of solid electrolytes is orders of magnitude lower than that of liquid electrolytes ($> 10^{-3}$ S/cm). Although some recent studies have revealed that specific ceramic electrolytes delivered high ionic conductivities at the magnitude of $10^{-3}$ S/cm\textsuperscript{[26]}, the demanding processing of the ceramics remains another issue. Meanwhile, the poor interfacial contact between the electrodes and solid electrolytes brings about high interfacial resistance for ion-conduction. These two critical issues result in poor electrochemical performance and have severely limited the broad applications of solid electrolytes.

1.2.4 Solution to improving capacity: lithium-sulfur (Li-S) battery

1.2.4.1 Li-S battery

In the studies of high-capacity electrodes, sulfur has drawn considerable attention due to its advantages in high theoretical energy density (2600 Wh/kg), high theoretical specific capacity (1675 mAh/g) and low cost.\textsuperscript{[27]} The high capacity of Li-S batteries originates from the phase-transformation chemistry of elemental sulfur ($S_8 + 16 Li \leftrightarrow 8 Li_2S$). This allows more Li ions to be accommodated as compared with the metal oxide cathodes of current LIBs. As illustrated in Figure 1.3 (a) and (b), for the intercalation-type LIBs, only one Li ion can be accommodated per transition metal element when the material is fully lithiated.\textsuperscript{[28]} The transition from intercalation-type electrodes to sulfur helps to improve the capacity and substitute the expensive and toxic metal oxide compounds.
Figure 1.3. Schematic illustration of (a) intercalation reaction-based LIBs and (b) conversion reaction-based Li-S batteries.[28]

As shown in Figure 1.3 (b), typical Li-S batteries comprise a sulfur cathode, a Li metal anode, a separator and an organic liquid electrolyte. In this cell configuration, sulfur is first reduced to Li$_2$S in discharging process and oxidized to sulfur in charging process. Another configuration replaces sulfur cathode with Li$_2$S, which is applicable in a Li anode-free battery to improve safety. In this case, Li$_2$S cathode is fully discharged, such that the cell needs to be charged first. For both cell configurations, the electrochemistry is complicated and involves multi-step reactions. The voltage profile of Li-S batteries shown in Figure 1.4 (a) indicates that the electrochemical reaction includes two or three stages depending on the electrolytes.[28] In discharging process (Figure 1.4 (b)), octasulfur (cyclo-S$_8$) is first reduced with ring opening, resulting in the formation of high-order lithium polysulfides (Li$_2$S$_x$, 4 ≤ x ≤ 8). The discharge plateau at around 2.3 V is attributed to this process. The high-order lithium polysulfides are further reduced by discharging to form low-order lithium polysulfides (Li$_2$S$_x$, 1 < x < 4), which corresponds to the lower discharge plateau of
2.1 V. In charging process, Li$_2$S is oxidized to S$_8$ with forming a series of lithium polysulfides, which gives rise to reversible electrochemical reactions and overlapped charging plateaus.$^{[29]}$

Figure 1.4. Voltage profile of a Li–S battery indicating the phase-transformation of polysulfides.$^{[30]}$ (b) Electrochemical reactions of sulfur-related species with Li and the corresponding reaction potential.

1.3 Overview of electrolytes of LIBs

1.3.1 Liquid electrolytes

A. Organic liquid electrolytes

Organic liquid electrolytes (OLEs) are the most classic electrolytes that are widely used in current LIBs owing to their remarkable ionic conductivity (> $10^{-3}$ S/cm) and good wetting ability. OLEs are composed of Li salts dissolved in organic solvents that are mostly carbonate esters, such as ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), diethyl carbonate (DEC), 1,2-dimethoxy ethane (DME), 1,3-dioxolane (DOL) and ethyl methyl carbonate (EMC), etc. The fundamental requirements for electrolyte solvents include high solubility of Li salts, low viscosity for facilitating ion-transport, wide operation window, safety and so forth.
Common Li salts include LiPF$_6$, LiTFSI, LiClO$_4$, LiFSI, etc. OLEs have an oxidation potential of about 4.5 V and a reduction potential near 1.0 V (vs. Li/Li$^+$). The combinations of Li salts and solvents play a critical role in the electrochemical performance, especially in present battery community pursuing high energy/power densities. Taking Li-S batteries for example, it is well-established that single solvent is not able to meet all the requirements for electrolytes, as Li-S batteries possess complex electrochemistry and involves multiple phase-trans formations of polysulfides. Researchers have revealed that DME has high solubility of polysulfides and kinetics for transforming polysulfides but is reactive with Li metal anode; DOL helps to stabilize SEI layer but shows low solubility of polysulfides. Therefore, a mixed solvent of DME/DOL shows much better capacity and cycling performance as compared with single solvent system.$^{[31]}$

Although OLEs have gained great success over the past few decades, the safety and thermal/electrochemical stabilities of OLEs need to be improved. Organic solvents are flammable, leading to the possibility of combustion and even explosion. In specific conditions such as thermal runaway, the violent exothermic reaction generates combustible gases reacting with oxygen from the broken-down cathode materials, eventually giving rise to combustion or explosion of the batteries. Considerable efforts have been made to modify the OLEs, such as adding additives (e.g. redox shuttles, flame retardants, etc.) and developing new Li salts or organic solvents with better stability.$^{[32]}$ For instance, to improve the electrochemical stability of OLEs against high voltage, organic fluoro-compounds have drawn considerable attention. This is because fluorinated molecules show much higher oxidation potential resulting from the strong electron-withdrawing effect of fluorine.$^{[31]}$ For instance, Zhang et al.$^{[33]}$ revealed that a mixture electrolyte of 1.2 M LiPF$_6$ in fluorinated cyclic carbonate(F-AEC)/fluorinated linear carbonate (F-EMC)/fluorinated ether (F-
EPE) showed much better performance in comparison of an EC/EMC electrolyte for LiNi_{0.5}Mn_{1.5}O_4 cathode.

**B. Ionic liquid electrolytes**

**Table 1.1** Comparison of different types of ionic liquid electrolytes

<table>
<thead>
<tr>
<th>Type of ILs</th>
<th>Cation</th>
<th>Anion</th>
<th>Viscosity</th>
<th>Ionic conductivity</th>
<th>Electrochemical stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazolium-based</td>
<td><img src="image" alt="Imidazolium structure" /></td>
<td><img src="image" alt="Imidazolium structure" /></td>
<td>Low</td>
<td>High (&gt; 10^{-3} S/cm)</td>
<td>Low (ca. 4 V)</td>
</tr>
<tr>
<td>Quaternary ammonium-based</td>
<td><img src="image" alt="Quaternary ammonium structure" /></td>
<td><img src="image" alt="Quaternary ammonium structure" /></td>
<td>High</td>
<td>Low</td>
<td>High (&gt; 5 V)</td>
</tr>
<tr>
<td>Pyrrolidinium and piperidinium-based</td>
<td><img src="image" alt="Pyrrolidinium structure" /></td>
<td><img src="image" alt="Pyrrolidinium structure" /></td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

Ionic liquids (ILs) are molten salts at room temperature with non-volatile and non-flammable properties. They can be employed as the electrolytes for LIBs when Li salts are introduced. As compared with conventional OLEs, ILs possess significant advantages in thermal stability (> 300 °C)^{[32]}^, making them promising candidates for safer LIBs. In addition, ILs present
many attractive attributes such as relatively high ionic conductivity, wide electrochemical stability window up to 6 V, high solubility of inorganic/organic compounds, good wetting behavior with electrodes.\textsuperscript{[34]} However, ILs exhibit much higher viscosities than that of conventional OLEs, resulting in reduced ionic conductivities in comparison. Moreover, the high cost of ILs has limited the broad applications of them.

Various combinations of cations and anions lead to many types of ILs with different properties. Basically, several categories of ILs are intensively studied, including imidazolium based, quaternary ammonium based, pyrrolidinium and piperidinium based, etc. in the basis of the cations. Table 1.1 indicates some representative ionic liquids for electrolyte applications and compares their important properties. It can be seen that imidazolium based ILs show low viscosities at room temperature leading to decent ionic conductivities that are usually higher than $10^{-3}$ S/cm. However, this type of ILs suffers from narrow electrochemical stability window below 4 V. By contrast, quaternary ammonium based ILs show good electrochemical stability up to 5 V, but the high viscosity deteriorates the ionic conductivity. It seems that pyrrolidinium and piperidinium based ILs possess relatively high ionic conductivity and electrochemical stability simultaneously.

1.3.2 Solid electrolytes

A. Inorganic electrolytes

Inorganic electrolytes including ceramic, glassy and glassy-ceramic types, present attractive physicochemical and electrochemical properties such as high elastic modulus, good electrochemical/thermal stabilities and high Li$^+$ transference number.\textsuperscript{[35]} Specifically, their elastic modulus ranges from tens to hundreds gigapascals, which is robust enough to suppress the growth
of Li dendrites. At the same time, inorganic electrolytes usually possess wide electrochemical stability window > 5 V, making them suitable for high-voltage LIBs. They also exhibit remarkable thermal stability even up to 900 °C[36] against Li metal anode, which effectively enhances the safety of the batteries.

The ion-conduction mechanism for inorganic electrolytes is dependent on passing periodic bottleneck, which can be controlled by substitution with ions with different radii in the lattice for sizing the bottleneck.[37] For example, a large doping ion can expand the lattice size and thereof the bottleneck size, which reduces the activation energy and improves the ionic conductivity. Meanwhile, the ion-conduction of inorganic electrolytes is decoupled with the structural relaxation, which indicates that they are generally single ion-conductors with Li\(^+\) transference numbers close to 1. Common inorganic electrolytes include garnet-type, LISICON (lithium super ionic conductor)-type, phosphate-type, perovskite-type, sulfide-type, etc. The ionic conductivities of the various types of inorganic electrolytes range from 10\(^{-10}\) to 10\(^{-2}\) S/cm at room temperature based on the ion-conduction mechanism and the lattice structure (ion vacancy and size).[38] Despite that inorganic electrolytes exhibit excellent properties as introduced above, the practical use of them is still limited by three main reasons: (1) most inorganic electrolytes suffer from lower ionic conductivity compared with liquid electrolytes; (2) the processing of inorganic electrolytes usually involves high pressure/temperature, which is demanding and costly; (3) the poor processability and brittleness of them limit their applications.

**B. Solid polymer electrolytes**

Another significant type of solid electrolytes is solid polymer electrolyte (SPE). SPEs refer to the solid polymers that are able to transport ions such as Li ions. SPEs are believed to be the
most promising candidates to replace liquid electrolytes for applications of wearable electronics and microelectronics, because of their remarkable advantages such as excellent mechanical properties, high safety and good flexibility.\textsuperscript{[39,40]} In addition, it is also found that SPEs are of great potential to suppress the growth of lithium dendrites due to their high modulus.\textsuperscript{[41,42]} Similar to the composition of liquid electrolytes, for SPEs, the polymer hosts act as “solid solvents” that dissolve Li salts. The Li salts can be dissociated by the polymer hosts due to the coupling interaction between the electrolyte ions and the polymer hosts, and thus, the ions are movable in the free volume of the polymer hosts. The most critical property for electrolytes is their ionic conductivity. It is generally accepted that the ionic conductivity of SPEs is confined in the amorphous phase of the polymer hosts above the glass transition temperature. Due to the long-chain effect and slow segment movement, the ionic conductivity of SPEs (< 10\textsuperscript{-4} S/cm at room temperature) is far lower than that of the liquid electrolytes, which severely hinder the practical applications of SPEs.

Over the past years, research efforts have been mainly concentrated on many kinds of polar polymers such as poly(ethylene oxide) (PEO)\textsuperscript{[43–45]}, poly(propylene oxide) (PPO)\textsuperscript{[46–48]}, polyacrylonitrile (PAN)\textsuperscript{[49–51]} and so on. The most classic SPE system is PEO-based electrolytes. PEO is a typical semi-crystalline polymer and shows very good solubility for various Li salts. The typical ionic conductivity of PEO-based SPEs is in the range of 10\textsuperscript{-8} – 10\textsuperscript{-4} S/cm at room temperature. PEO can form complexes with Li salts primarily due to the coupling interactions between Li ions and oxygen atoms of the PEO chains.\textsuperscript{[52–54]} On one hand, the strong coupling interaction facilitates the dissociation of Li salts. However, on the other hand, it impedes the ion transport simultaneously. The coupling effect between PEO and Li ions can be well reflected by several aspects. For instance, the ionic conductivity can be increased by decreasing the molecular weight of PEO or by increasing flexibility of PEO chains via adding plasticizers.\textsuperscript{[55–57]}
1.3.3 Gel polymer electrolytes

All solid LIBs with SPEs have never reached the stage of large-scale commercialization due to the unsatisfactory ionic conductivity and poor interfacial property of SPEs. Concerned by these critical issues, people have paid increasing attention to gel polymer electrolytes (GPEs), in which advantages of both liquid electrolytes (e.g. high ionic conductivity, good interfacial property) and SPEs (e.g. good mechanical properties, high safety) can be taken. Although the introduction of a liquid component inevitably deteriorates the mechanical properties, the combination of the attributes from different states of components is still an attractive approach to achieving moderate to high performances overall. Therefore, GPEs are still considered as appropriate electrolytes for fabrication of advanced LIBs with enhanced flexibility and safety.

Various polar polymers have been studied as the hosts for fabrication of GPEs, such as PEO\textsuperscript{[56,58]}, poly(vinylidene fluoride) (PVDF)\textsuperscript{[59,60]}, poly(methyl methacrylate) (PMMA)\textsuperscript{[61,62]} and so forth. These polymers usually have good affinity with liquid electrolytes. It is also noted that in addition to OLEs, new electrolytes such as ionic liquid electrolytes have also been of great interest for fabrication of GPEs recently. Studies on GPEs are mainly focusing on optimization of their structures and compositions to enhance ionic conductivity, mechanical performance, interfacial property, etc. For GPEs, to achieve high ionic conductivity and good mechanical properties is the primary challenge. The liquid component induces swelling of the polymer host, and therefore the mechanical properties of GPEs are unavoidably sacrificed to some degree. The key to alleviate this issue is to design structures that can adsorb large amount of liquid and meanwhile retain good structural integrity.
1.3.4 Advantages and disadvantages of various electrolytes

To gain deep insights on the merits and demerits of various electrolytes, the important properties for each type of electrolytes are summarized and compared in Table 1.2. For electrolyte applications, ionic conductivity is the priority property and mechanical performance becomes important for specific battery design. As shown, liquid electrolytes including OLEs and ILs show superior performances in ionic conductivity and interfacial properties; nonetheless they exhibit extremely poor mechanical properties. Solid electrolytes (inorganic electrolytes and SPEs) have advantages in mechanical properties, stabilities and safety but their critical drawbacks are low ionic conductivity and poor interfacial properties. GPEs present moderate performances in these properties. Therefore, the main tasks for liquid-based electrolytes is to improve the safety and stabilities. For solid electrolytes, the primary challenge is improving the ionic conductivity and

Table 1.2 Comparison of important properties of various types of electrolytes for LIBs

<table>
<thead>
<tr>
<th>Property</th>
<th>Organic liquid electrolytes</th>
<th>Ionic liquid electrolytes</th>
<th>Inorganic electrolytes</th>
<th>Solid polymer electrolytes</th>
<th>Gel polymer electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity</td>
<td>High (&gt; 10^3 S/cm)</td>
<td>Moderate to high (close to 10^3 S/cm)</td>
<td>Low</td>
<td>Low (&lt; 10^-4 S/cm)</td>
<td>Moderate</td>
</tr>
<tr>
<td>Mechanical performance</td>
<td>Poor</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Moderate</td>
</tr>
<tr>
<td>Electrochemical stability</td>
<td>Poor</td>
<td>Poor to moderate</td>
<td>Good</td>
<td>Good</td>
<td>Moderate</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Moderate</td>
</tr>
<tr>
<td>Interfacial properties</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Poor</td>
<td>Moderate</td>
</tr>
<tr>
<td>Safety</td>
<td>Poor</td>
<td>Moderate</td>
<td>Good</td>
<td>Good</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
interfacial properties to ensure good contact between electrodes and solid electrolytes, while for GPEs enhancing mechanical properties is the main task.

1.4 Solid polymer electrolytes (SPEs) for LIBs

1.4.1 Structures of SPEs

Driven by the booming development of flexible and wearable electronics, SPEs have received tremendous attention owing to their superior performances in mechanical performance, safety, processability and design flexibility. As introduced in Section 1.2.2.2, SPEs are mixtures of polymer matrices and Li salts. Specially, a SPE usually contains a Lewis base and behaves like a “solid solution” in which ions are solvated and dissociated. Therefore, such solvated ions are movable within the space provided by the free volume of the polymer host. The polymer chains/segments become free above glass transition temperature that results in ionic conductivity. To satisfy the needs for practical applications, such significant properties must be accomplished: high ionic conductivity, good mechanical/interfacial properties and good electrochemical/thermal stabilities. Among them, ionic conductivity is the primary property for an electrolyte. Typically, the ionic conductivity of SPEs is in the range of $10^{-8}$~$10^{-4}$ S/cm that is well below that of liquid electrolytes ($> 10^{-3}$ S/cm).

The ion-transport for SPEs is dependent on the segment relaxation of the polymer hosts. Figure 1.5 illustrates the widely-accepted ion-transport models for SPEs. Specifically, the Li ions are coordinated with the polymer chains; namely, Li ions form complexes with ether oxygen atoms of PEO. With continuous process of breaking/forming coordination bonds, Li ions are transported via intrachain/interchain hopping. Similarly, the hopping of Li ions can also occur in the form of ion clusters with polymer chains as anchor sites.
Figure 1.5. Mechanisms of ion transport for SPEs via intrachain/interchain ion or ion cluster hopping.[52]

1.4.2 Strategies for improving SPE performance

The most challenging and critical issue for SPEs is to improve their ionic conductivity to approach the level of liquid electrolytes. Figure 1.6 illustrates the distribution states of the Li ions in SPEs that are determined by the physical properties of the polymer hosts and are very critical affecting the dynamics of the transport of Li ions. Specifically, Li ions distributed in amorphous phase are able to migrate more freely compared with those in crystalline phase. In addition, nanoparticles introduce special polymer-nanoparticle interphases for distributing Li ions,
Figure 1.6. The distribution of Li ions in SPEs in different states: (a) in amorphous state, (b) in crystalline state and (c) around nanoparticle interphases.

Due to the fact that the transport of Li ions is associated with the motion of polymer molecules, the primary solution for improving the ionic conductivity is to depress the crystallization of the polymers to create amorphous phase as much as possible. Thus far, various strategies have been investigated such as introducing nanoparticles (e.g. Al$_2$O$_3$\cite{63,64}, TiO$_2$\cite{65,66}), adding plasticizers\cite{56,57}, blending with polymers\cite{45,67} and so forth. The primary purpose of these strategies is to increase the percentage of amorphous phase in the polymer hosts. Among these approaches, addition of nanoparticles is found to be very attractive because of several aspects. Firstly, the ion transport can be facilitated due to the conductive interfaces formed between the polymer matrix and nanoparticles, and due to the formation of Lewis acid-base interaction between the electrolyte ions and the nanoparticles. Secondly, the nanoparticles can act as reinforcement additives to enhance the mechanical properties that are deteriorated by reduced crystallinity of the polymer hosts. The effects of ceramic fillers\cite{44,68}, zeolites\cite{69} and hybrids\cite{70} on SPEs have been well investigated. It is also established that addition of nanofillers may improve the compatibility between electrolyte and lithium electrode as well as thermal/electrochemical stabilities of the electrolytes. Moreover, the nanofillers can be designed with various dimensions and functionalities to involve in the ion conduction. For example, some fillers having high aspect ratio such as fiber-like structure\cite{71} can easily construct continuous conductive networks. At the same time, some fillers can be chemically modified to introduce atoms (e.g. Boron\cite{72}) that can actively interact with ions in order to increase ionic conductivity and Li$^+$ transference number that is defined as the fraction of electric current contributed by Li ions.
Copolymers with conductive blocks are another type of promising candidates for high-performance SPEs. Specifically, the conductive block (e.g. EO block) is responsible for the ion transportation, and meanwhile the other blocks, such as polyethylene (PE) or polystyrene (PS), enable to form 3D frameworks to provide strong mechanical strength. Their properties can be precisely patterned by adjusting simultaneously their block fractions and polymer architectures. It is usually found that the ionic conductivity and mechanical properties are significantly dependent on the specific microstructures of the blocks. For instance, Bouchet et al.\cite{73} reported a PS-PEO-PS block polymer electrolyte, and found that compared with the linear PEO, comb PEO showed slightly better ionic conductivity owing to absence of PEO crystallization, but the linear PEO presented the best compromise between high conductivity and good mechanical properties. Although copolymers enable a fine design of ion-conduction pathways, the mechanism of the ion-conduction in the conductive blocks is generally the same as that of conventional SPEs. Therefore, the ionic conductivity of copolymer-based SPEs is usually at the same level as it is for common SPEs.

1.4.3 Bio-based SPEs

In addition to synthetic polymers, natural biomaterials enabling to dissolve ionic salts have been recently studied for SPEs such as gelatin, agar, starch, chitosan, etc. as summarized in Table 1.3. Due to the abundance of the natural polymers in environment and the aim to develop sustainable ESDs, they become promising substitutes for synthetic polymers. As compared with synthetic polymers, biopolymers, owing to their intrinsically complicated molecular structures, obtain much better mechanical strength. Current studies on bio-based SPEs are following the traditional direction on synthetic polymers, in which the biomaterials are serving as hosts as well
to solvate the salts. For most of the reported work, plasticizing the biopolymers is the main route for enhancing the ionic conductivity. Their ionic conductivity is reported to be in the range of $10^{-8} \text{~to~} 10^{-4} \text{ S/cm}$ at the similar level of conventional synthetic SPEs. However, the vast natural resources and variety of functional structures of the biomolecules supply expansive space for in-depth studies to exploit the undeveloped functionalities of them. In addition, such exploration on bio-based SPEs has potentially enlarged the opportunities for them towards the design of “greener” and safer ESDs.

**Table 1.3** State-of-the-art bio-based solid electrolytes

<table>
<thead>
<tr>
<th>Material</th>
<th>Salt</th>
<th>Enhancing method</th>
<th>Ionic conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>LiCF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Plasticizing</td>
<td>$1.07 \times 10^{-5} \text{ (30 °C)}$[69]</td>
</tr>
<tr>
<td></td>
<td>LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Polymer graft</td>
<td>$2.08 \times 10^{-5} \text{ (40 °C)}$[74]</td>
</tr>
<tr>
<td>Starch</td>
<td>LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Plasticizing</td>
<td>$1.1 \times 10^{-4} \text{ (30 °C)}$[75]</td>
</tr>
<tr>
<td></td>
<td>NH&lt;sub&gt;4&lt;/sub&gt;I</td>
<td>N/A</td>
<td>$2.4 \times 10^{-4} \text{ (30 °C)}$[76]</td>
</tr>
<tr>
<td>Chitosan</td>
<td>LiCF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Plasticizing</td>
<td>$5.0 \times 10^{-6} \text{ (25 °C)}$[77]</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;COONH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>N/A</td>
<td>$2.87 \times 10^{-4} \text{ (25 °C)}$[78]</td>
</tr>
<tr>
<td>Agar</td>
<td>LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>N/A</td>
<td>$3.53 \times 10^{-8} \text{ (25 °C)}$[79]</td>
</tr>
<tr>
<td></td>
<td>LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Plasticizing</td>
<td>$6.5 \times 10^{-5} \text{ (25 °C)}$[80]</td>
</tr>
<tr>
<td>Gelatin</td>
<td>LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Plasticizing</td>
<td>$1.0 \times 10^{-4} \text{ (25 °C)}$[81]</td>
</tr>
<tr>
<td></td>
<td>Li+MMT</td>
<td>N/A</td>
<td>$1.44 \times 10^{-6} \text{ (25 °C)}$[82]</td>
</tr>
</tbody>
</table>
1.4.4 Critical challenge: trade-off between ionic conductivity and mechanical properties

Although many abovementioned strategies have made significant progress for improving the ionic conductivity of SPEs, the mechanical properties are reduced. The key issues of SPEs are fundamentally determined by the ion-transport mechanism that is coupled with the relaxation of the polymer segments. Ionic conductivity of SPEs has long been viewed as confined to the amorphous phase above the glass transition temperature. A high ionic conductivity is critically required, but the ionic conductivity of SPEs is far poorer than that of liquid electrolytes to meet the needs for practical applications. In addition to high ionic conductivity, good mechanical properties are also significantly required for SPEs. Mechanically strong SPEs warrant them to survive from the extremely high compression pressure applied in fabrication process and to prevent the growth of Li dendrites from impaling the SPEs during cycling processes. However, to increase the ionic conductivity by creating more relaxed molecule chains/amorphous phase, the mechanical properties will correspondingly and inevitably deteriorate. The routes discussed in Section 1.3.2 for improving the ionic conductivity such as plasticizing and blending will give rise to a loss of mechanical properties. In other words, the trade-off between ionic conductivity and mechanical properties always exists that has limited the further improvement of SPEs. It is therefore very encouraging to explore new polymer systems with greater potentials to fully improve their ionic conductivity and achieve desirable mechanical properties. Meanwhile, although bio-based materials hold great promise for solving this trade-off behavior due to their intrinsically complex interactions with ions, the understanding of their functionalities/structures and their interactions with ions are still superficial. They have simply been replacing the role of synthetic polymers by acting as polymer hosts with plasticizer/nanoparticles introduced. Unfortunately, the issues associated with coupled ion transport still exist. It is expected that the actual situation of the ions
in the biomaterials is more complicated than that in simple synthetic polymers. It so far lacks an in-depth scientific understanding of the interactions among the rich functional groups and ions. The various functional groups are potentially reactive with certain ions and able to form interesting structures with them.

1.5 High-energy batteries: Li-S batteries

1.5.1 Critical challenges for Li-S batteries

Although Li-S batteries hold great promise for next-generation Li batteries as introduced in Section 1.2.3.1, they are facing several critical challenges in both materials and system levels:

(1) Insulating nature of sulfur and Li$_2$S: Both the cathode materials, sulfur and Li$_2$S, are non-conductive materials, which limits them from accepting electrons from the current collectors. Therefore, a high loading of conductive agents is added to the electrodes to ensure smooth charging/discharging, which sacrifices the energy density substantially.

(2) Large volume change of cathodes: Sulfur cathodes experience a large volume change of about 80% when it converts to Li$_2$S (densities of sulfur and Li$_2$S are 2.03 and 1.66 g/cm$^3$, respectively).$^{[28]}$ The notable volume change damages the cathode architecture in charging/discharging processes, which severely deteriorates the electrochemical performance. At the same time, it also brings about challenges for realizing high loading of sulfur for meeting the commercialization demands.

(3) Shuttle effect of polysulfides: Sulfur and polysulfides are easily dissolved in organic liquid electrolytes. This not only consumes the sulfur active materials, but also results in the diffusion of polysulfides from the cathode to anode that is also known as shuttle effect (Figure 1.7). In specific, the high-order polysulfides are reduced to low-order ones at the Li anode surface
and then move back to the cathode being re-oxidized to form high-order polysulfides in charging state. The shuttle effect prolongs the charging process, decreasing the Coulombic efficiency. Meanwhile, Li metal anodes can be corroded by polysulfides and even passivated by the deposited insoluble Li₂S/Li₂S₂. Shuttle effect is the main reason for deterioration of the battery performance.

(4) Self-discharge: Self-discharge is a common issue in Li-S batteries, mainly resulting from the shuttle effect. In rest state, the dissolved sulfur species migrate to the Li anode side due to a concentration gradient, which are reduced by the Li metal. As a result, the upper discharge plateau disappears, and the open-circuit voltage decreases with a capacity loss.

(5) Issues with Li metal anode: The utilization of Li metal as the anode brings about three issues: i. The interaction between Li metal and liquid electrolytes consumes the liquid electrolytes and leads to the formation of unstable solid electrolyte interface (SEI) layer; ii. The uncontrollable Li dendrite growth poses safety issues; iii. Li metal anode can be corroded and passivated by polysulfides.

![Figure 1.7](image_url) Schematic illustration of shuttle effect mechanism in Li-S batteries based on liquid electrolytes.[83]
1.5.2 Binder materials for improving performance of Li-S batteries

A. Binder materials

![Schematic illustration of the microstructure changes of sulfur cathodes with a multifunctional robust binder as compared with a traditional binder.](image)

**Figure 1.8.** Schematic illustration of the microstructure changes of sulfur cathodes with a multifunctional robust binder as compared with a traditional binder.

Binder materials are the only “soft” materials that glue the active materials and conductive agents together into an electrode configuration. Despite of their low loading in electrodes (usually < 10 wt%), binders play a critical role in the microstructures and mechanical properties of the electrodes. Primary binders such as polyvinylidene fluoride (PVDF), carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), etc. have gained significant commercial success. These primary binders are able to offer sufficient adhesion and mechanical properties for conventional electrodes but fail to render good performance in Li-S batteries. This is because sulfur cathodes experience notable volume expansion of ca. 80% in electrochemical reactions and dissolution of sulfur-related species such as polysulfides as introduced above. These two issues lead to severe
pulverization of sulfur cathodes, which further deteriorates the battery performance as shown in Figure 1.8. In this context, advanced binders with functions beyond mechanical support are in critical need for Li-S batteries. For instance, as shown in Figure 1.8, a functional and robust binder being able to buffer the large volume change and suppress the diffusion of polysulfides will be of great significance for enhancing the performance of Li-S batteries.

Rationally designing advanced binders for sulfur cathodes takes several aspects into consideration: mechanical properties, polysulfide adsorption and conductivity. Specifically, mechanical properties are critical for sustaining the volume deformation of sulfur and polysulfide adsorption ability helps to reduce the loss of sulfur active materials and the shuttle effect. In addition, ionically-/electrically-conductive binders benefit the charge-transfer of the batteries. Various mechanically strong binders for sulfur cathodes have been reported in addition to PVDF, such as polytetrafluoroethylene (PTFE), guar gum, xanthan gum, polyacrylonitrile (PAN) and so on.\[84–86\] Additionally, a large number of binders with strong ability for anchoring polysulfides has been investigated. They are usually polar polymers such as polyethylene oxide (PEO), gelatin, polyvinylpyrrolidone (PVP), polyacrylic acid (PAA), polyethylenimine (PEI), etc., which show strong dipole-dipole interactions with polysulfides.\[87–90\] The abovementioned binders are “dead” components in electrodes, which are not involved in electrochemical reactions. In contrast, conductive binders are of great interest, as they promote the electrochemical reactions by facilitating the transport of ions or electrons. Conductive binders mainly include poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), Nafion, polypyrrole (PPy), polyaniline (PANI), etc.\[91–94\]
B. Critical challenges for developing advanced binders

Designing advanced binder materials is imperative for achieving high-performance Li-S batteries. Previous studies have indicated that improving mechanical/adhesion properties, polysulfide regulation ability and conductivities is effective for enhancing the battery performance. Therefore, developing a multifunctional binder integrating high mechanical/adhesion properties, strong trapping of polysulfides and conductivities is believed to be promising for further improving the performance. For fabricating multifunctional binders, researchers have adopted many strategies such as polymerization, blending, cross-linking and so forth. Among them, polymerization can rationally and precisely design the binder structures and functionalities, while blending and cross-linking feature low cost and facile fabrication process. Moreover, owing to the large volume change of sulfur cathodes and dissolution of sulfur/polysulfides, it has been very challenging for achieving high sulfur loading, which limits the energy density of the Li-S batteries for practical use. In a nutshell, the critical challenges for the development of binder materials for sulfur cathodes are: (1) realizing multifunctional binders with high mechanical properties, good polysulfide trapping ability and conductivities via a facile and low-cost strategy; (2) achieving high sulfur loading for delivering an areal capacity comparative to commercial LIBs (> 4 mAh/cm²).

1.5.3 Interlayers for improving performance of Li-S batteries

A. Advanced interlayers

As shown in Figure 1.9 (a), the shuttle effect from dissolving of lithium polysulfides (Li₂Sₙ, n = 4 ~ 8) is one of the primary issues resulting in a rapid decay of capacity and low
Coulombic efficiency for Li-S batteries. The migration of polysulfides between the two electrodes will reduce the active surface area of Li metal anode due to side reactions between polysulfides and Li metal, as well as destroy the morphology of sulfur cathodes. To alleviate the shuttle effect, the interlayer or separator coating works as a filtering material for capturing polysulfides, such that polysulfides can be confined within the cathode region as illustrated in Figure 1.9 (b). When the interlayer is placed between the sulfur cathode and separator, it filters and immobilizes the dissolved polysulfides, but allows the diffusion of Li ions.

![Figure 1.9](image)

**Figure 1.9.** Schematic illustration of Li-S batteries with (a) a conventional separator and (b) an interlayer inserted between the sulfur cathode and separator.

The interlayers are fabricated in the forms of freestanding films or separator coatings that intimately contact the separators. Typically, the interlayer plays a role in anchoring and/or
converting dissolved polysulfides via two functional mechanisms: (1) blocking polysulfides diffusion, (2) enhancing conversion kinetics of polysulfides.\textsuperscript{[97]} In terms of the interlayer that simply blocks the polysulfides, intensive studies on conductive interlayers have been reported as the electron transfer is needed for conversion of polysulfides. The conductive interlayers are mainly based on carbon nanomaterials such as carbon black\textsuperscript{[98,99]}, carbon nanotubes\textsuperscript{[100,101]}, graphene\textsuperscript{[102,103]}, carbon nanofibers\textsuperscript{[104,105]}, etc. To further enhance the anchoring capability, tremendous efforts have been made to functionalize the interlayer materials to provide strong chemical or electrostatic interactions with the polysulfides. In this strategy, various nanomaterials such as metal oxides (i.e. \( \text{Al}_2\text{O}_3 \))\textsuperscript{[106]}, \( \text{ZnO} \))\textsuperscript{[107]}, heteroatom-doping carbon nanomaterials (i.e. N-doped carbon foam\textsuperscript{[108]}, N,S-doped graphene\textsuperscript{[109]}), metal organic framework\textsuperscript{[110]}, etc. and many kinds of functional polar polymers, i.e. polyacrylic acid\textsuperscript{[111]}, polyethylene glycol\textsuperscript{[101]}, polyvinylpyrrolidone\textsuperscript{[112]} have been demonstrated to show great trapping ability due to their strong chemical interactions with polysulfides. Meanwhile, researchers have also utilized electrostatic repulsion interaction to fabricate effective interlayers to reject the polysulfides, for example, montmorillonite-coated separator\textsuperscript{[113]} and sulfonated perfluoroalkyl ether group modified separator\textsuperscript{[114]}. In addition to above strategies, more recently some studies revealed that incorporating catalysts into the interlayer can significantly accelerate the sluggish electrochemical reaction kinetics of polysulfides especially at high current rates. To that end, diverse catalysts including \( \text{WS}_2 \)\textsuperscript{[115]}, \( \text{CoS}_2 \)\textsuperscript{[116]}, etc. have been incorporated and demonstrated to significantly improve the electrochemical performances, even though the catalytic mechanisms still remain unclear. Therefore, introducing an interlayer is a very promising approach to addressing the shuttle effect without sacrificing the intrinsic merits of the batteries, which can be readily combined with current battery technologies.
B. Critical challenges for high-performance interlayers

The design and fabrication of interlayers for trapping polysulfides in Li-S batteries have attracted considerable attention. It is believed that introducing specific materials (e.g. inorganic materials, polymers) showing strong interactions with polysulfides is a feasible approach for fabricating high-performance interlayers. In fact, a great number of studies have focused on creating advanced and new nanomaterials for more effectively capturing polysulfides. However, the roles that the interlayers play in transport of Li ions have been scarcely discussed. The introduction of a battery interlayer may result in additional resistance for ion-transport, which brings about the needs to understand the effects of interlayers in ion-transport in addition to trapping polysulfides. At the same time, there is a lack of instructive studies on design strategies of advanced interlayers and characterization methods for evaluating them. Therefore, developing advanced interlayers enabling strong adsorption of polysulfides and promotion of ion-transport is imperatively demanded. Further, all-inclusive characterizations of the interlayers are in great need for designing better battery interlayers.

1.6 Protein for energy storage

Proteins, as a category of the most important biomaterials, possessing four-level structures as shown in Figure 1.10. It is well known that proteins have rich functional groups derived from various kinds of amino acids, potentially bringing about unique interactions with ions (i.e. Li ions), polymers, etc. The unique properties of protein allow them to be suitable materials for energy storage applications. Particularly in electrolyte area, the good attributes make proteins act as matrices for SPEs or as advanced bio-fillers for enhancing conventional SPEs. At the same time, the special configuration of proteins may enable new ion-conduction pathways. Moreover, proteins
are a type of rigid bio-polymer due to the complex molecular structure and strong intra-/inter-chain interactions.\cite{117,118} Thus, the high modulus makes protein a proper material for fabricating robust SPEs. Our previous work by Ji et al.\cite{119} demonstrated the use of soy protein for fabricating ultra-elastic PEO-based SPEs with fully amorphous structure. The work indicated that soy protein enabled strong intermolecular interactions with PEO, such that the crystallinity was decreased, and the ionic conductivity was improved. In fact, there are some studies from other groups applying proteins for electrolyte applications. Most studies have reported using gelatin protein for solid or gel electrolytes\cite{81,82,120,121}, but other proteins are less intensively studied. In addition, a number of studies have reported using gelatin protein as the binder for sulfur cathodes\cite{89,122,123}, due to its superior adhesion properties and dispersing ability.

Figure 1.10. Four-level structures of proteins: primary, secondary, tertiary and quaternary structures.\cite{124}
1.7 Problem statement and research objectives

1.7.1 Problem statement

A. Solid polymer electrolytes (SPEs)

Owing to the coupled ion-conduction mechanism for SPEs, the increase of ionic conductivity usually accompanies with a decrease of mechanical properties. The trade-off between these two most critical properties, i.e. ionic conductivity and mechanical properties, is the primary issue that limits the further improvement of SPEs. In this context, there is a significant need for exploring new SPE systems being able to decouple the ionic conductivity from segment relaxation. Bio-based SPEs have complex molecular compositions and structures, which may lead to unique interactions with ions different from conventional synthetic polymers. Naturally, they have been considered to be promising SPE systems satisfying the above requirement. However, there is a lack of in-depth understanding of the interactions between the bio-based SPEs and ions. In other words, the ion-conduction mechanism for specific bio-based SPEs is not fully uncovered.

B. Binders for sulfur cathodes

Developing multifunctional binder materials integrating remarkable mechanical properties, good polysulfide trapping capability and proper conductivities is of great significance for advanced sulfur cathodes. Many strategies have been put forward to fabricate multifunctional binders and some of them have made significant progress. However, it has been very challenging to fabricate a multifunctional binder material via a simple and cost-effective way. Moreover, realization of high loading sulfur cathodes by rationally designing a binder still remains a critical challenge.
As introduced above, proteins obtain abundant functional groups including polar, non-polar and charged groups, potentially enabling them to adsorb polysulfides due to the strong dipole-dipole interactions. Although there are several studies from other groups reporting the use of gelatin as a binder for fabricating sulfur cathodes\textsuperscript{[122,123]}, the loading of sulfur cathodes was found to be very low (< 2 mg/cm\textsuperscript{2}); thus, the energy density was greatly limited. At the same time, these studies mainly focused on the improvement of the adhesion and mechanical strength by gelatin but lacked the understanding of the effects of proteins on electrode microstructures and polysulfide adsorption. Therefore, despite that applying protein as a multifunctional binder holds great promise for enhancing sulfur cathodes, the fabrication of high loading sulfur cathodes and understanding of the roles that protein plays in enhancing the electrochemical performance are still demanded.

C. Interlayers for Li-S batteries

Fabricating high-performance battery interlayers via applying nanomaterials/polymers with stronger polysulfide trapping ability is effective to reduce the loss of sulfur active materials and the shuttle effect. Nonetheless, due to the fact that the interlayers are additional components in the batteries, extra resistance for ion-transport might be generated, which has been seldom discussed. In other words, there is a lack of an understanding of the roles that the interlayers play in ion-transport, in addition to trapping polysulfides. At the same time, proposing cost-effective methods to comprehensively characterizing battery interlayers for gaining understanding of their roles in ion-transport has been a big challenge.
1.7.2 Research objectives

A. Solid polymer electrolytes (SPEs)

The primary objective of the proposed project is to fabricate advanced SPEs with high ionic conductivity and mechanical properties simultaneously by exploiting soy protein. The proposed projects include two research directions as illustrated in Figure 1.11: (1) fabrication of protein-based SPEs via using soy protein as the electrolyte matrix; (2) enhancing conventional SPEs by using soy protein as advanced filler. The specific tasks for both SPE systems include four stages: (a) Manipulate and optimize the structures of protein, which significantly affects interactions between protein and ions and thereby the ionic conductivity; (b) Characterize the properties of the SPEs and establish the structure-property relationships; (c) Study the ion-conduction mechanisms for the SPEs; (d) Proof-of-concept studies on the SPEs by demonstration in half coin cells.

![Figure 1.11](image)

**Figure 1.11.** Research objectives and specific tasks for achieving the targeted properties via fabricating two types of SPEs: bio-based SPEs and bio-filler enhanced SPEs.

B. Binders for sulfur cathodes

The overall objective of this project is to rationally design and fabricate a multifunctional binder based on protein via a facile and cost-efficient strategy, to realize high loading sulfur
cathodes. The proposed approach is to incorporate soy protein with polyacrylic acid (PAA) that is a commonly used binder for sulfur cathodes. With incorporation of PAA, the microstructures of the electrodes are expected to improve based on our previous study.\textsuperscript{[125]} Specific objectives are (1) to study the contributions of the multifunctional binder to the microstructures, mechanical properties, adhesion property and electrical conductivity of the resultant sulfur cathodes, (2) to uncover the effects of protein on adsorbing polysulfides and (3) to finally fabricate high loading sulfur cathodes.

C. Interlayers for Li-S batteries

The primary objective of the proposed project is to design and fabricate an advanced battery interlayer for simultaneously capturing polysulfides and promoting Li-transport. It is proposed that using gelatin protein as the binding material for fabricating conductive interlayers may bring about several benefits as gelatin protein plays multiple roles: (1) self-assembly agent for 3D porous nanostructure based on our prior study\textsuperscript{[126]}; (2) robust binding material for high mechanical properties; (3) active site for adsorbing polysulfides owing to protein’s various functional groups. Specific objectives include: (a) fabricate protein-based conductive interlayers via treating conductive fillers by protein; (b) comprehensively characterize the interlayers; (c) establish structure-property-performance relationship; (d) study the protein-polysulfide interaction mechanism; (e) propose a design model for advanced battery interlayers.
1.8 Dissertation structure

Figure 1.12. Schematic of the dissertation structure.

As shown in Figure 1.12, this dissertation consists of the following sections. Chapter 1 is the introduction of overview of LIBs, components of LIBs and development trends for advanced next-generation batteries. The critical challenges faced by researchers currently and research objectives are also described in Chapter 1. Chapters 2 to 4 include the studies of SPEs for improving the safety of LIBs. Specifically, Chapter 2 is the study and fabrication of protein-based SPEs as well as the ion-conduction mechanism studies of protein. This study lays the foundation for realizing advanced solid electrolytes by taking advantage of protein. Chapters 3 and 4 are the studies of hybrid protein/ceramic nanoparticles or nanowires for simultaneously improving the ionic conductivity and mechanical properties of conventional SPEs. Chapters 5 and 6 focus on developing a high-capacity battery system: Li-S battery. Chapter 5 is the study of protein-based
multifunctional binder for achieving high loading sulfur cathodes, while Chapter 6 includes the study of protein nanofilter as an interlayer for trapping polysulfides and promoting Li-transport in Li-S batteries. Chapter 7 is the summary of all the research conclusions and the outlook for fabrication of advanced batteries by adopting proteins.
CHAPTER 2

PROTEIN-BASED SOLID ELECTROLYTES WITH DECOUPLED ION-TRANSPORT

2.1 Introduction

Solid electrolytes are becoming one of the most important components in electrochemical devices due to the superior stability and safety properties. Good electrochemical and mechanical properties are required for practical applications of a solid electrolyte. However, in conventional polymer electrolytes or solid polymer electrolytes (SPEs) the ion transport is dominated by a coupled process, which is responsible for the low transference number and deteriorated modulus with the enhancement of ionic conductivity. In a SPE, both cations and anions of the salts are mobile, and the motion of the cations is highly coordinated by the polymer chains. As a result, the ion transport is strongly coupled with the local segmental motion of polymer chains in amorphous state above the glass transition temperature. Some strategies, such as addition of plasticizers and blending with other polymers, have been employed to increase the mobility of the polymer chains, and thus to improve the ionic conductivity. However, the corresponding mechanical properties were significantly reduced because of the increase in molecule mobility that leads to the improvement in ionic conductivity. Another important issue with the traditional SPEs is the low transference number (~ 0.4) caused by the unconstrained motion of the anions.

Proteins are natural polymers made out of a series of amino acids covalently linked through peptide bonds. Compared with the synthetic polymers, proteins in general are compositionally and
structurally much more complex. Therefore, utilizing protein as the polymer matrix and exploiting its functional groups through proper manipulation of its structures to achieve high-performance solid electrolytes are not only scientifically intriguing but also technically challenging. Recently, some protein (such as gelatin[^81][^121]) has been reported as the matrix for polymer electrolytes. Plasticizers have been added to improve ionic conductivity; therefore, the issues associated with coupled transport mentioned above still exist, most likely due to a lack of fundamental understanding of the protein-ion interactions and transport mechanisms in protein-based electrolytes. In this study, we present a systematic investigation of a solid-state soy protein (SP)-based electrolyte. An electrolyte with both excellent electrochemical and mechanical properties is achieved. Simulations have been performed to uncover the detailed molecular interactions and ionic transport mechanisms.

2.2 Experimental

2.2.1 Electrolyte preparation

As shown in Figure 2.1, soy protein (SP) isolate powders (Archer Daniels Midland Co.) were first denatured in a mixed solvent (80 wt% acetic acid, 20 wt% deionized water) in an oil bath under stirring at 95 °C for 1 hour to get a semi-transparent yellowish solution. It is noted that prior to adding SP powders, the solvent was preheated to 95 °C in the oil bath. The concentration of denatured SP (d-SP) was 3 wt%. The d-SP solution was cooled down at room temperature for 30 minutes. Then, a varying loading of LiClO$_4$ was added into the cooled d-SP solution and stirred for ca. 10 minutes until LiClO$_4$ was completely dissolved to obtain the d-SP/LiClO$_4$ solution. At the same time, polyethylene oxide (PEO) solution with a concentration of 1.6 wt% was prepared by dissolving PEO powders (Mw = 5,000,000 g/mol, Sigma Aldrich) in deionized water under
vigorous stirring. Then, PEO/LiClO$_4$ solution was prepared by dissolving a certain amount of LiClO$_4$ according to a mole ratio of oxygen atom of PEO to lithium ion, 8:1 (the weight ratio of PEO to LiClO$_4$ was 3.3:1). Afterwards, $d$-SP/LiClO$_4$ solution was blended with a small amount of PEO/LiClO$_4$ solution to prepare protein-based electrolyte. The weight ratio of $d$-SP to PEO was kept constant to be 85:15. After mixing for 30 minutes under stirring, the solutions were casted onto aluminum foil by using a Dr. Blade. Then, the samples were dried under different evaporation temperatures, including 25, 40, 50, 60 °C, for 16 hours. The thickness of the films was measured by a digital micrometer and was made consistent ~ 40±2 µm. The water content of the sample was measured by thermogravimetric analysis (TGA). Eventually the water content of the samples was found to be very similar that was in the range of 3 ~ 4 wt%.

![Figure 2.1](image-url)  
**Figure 2.1.** Fabrication process of protein-based solid electrolytes with controlling the loading of lithium salt and evaporation temperature for removing the solvents.

### 2.2.2 Molecular simulations

All MD simulations were performed using GROMACS package 4.3.1$^{[130]}$. The GROMOS 53A6 force field was applied to the protein$^{[131]}$; SPC model was chosen for water molecules; The interaction parameters and partial charges for acetic acid molecules were taken from the OPLS-AA library$^{[132]}$; AMBER force field was adopted for Li$^+$ ions and the parameters of the perchlorate ions were taken from Baaden et al.$^{[133]}$ The missing amino acids of the protein have been identified
and superimposed using Swiss program\textsuperscript{[134]} (http://swissmodel.expasy.org/). Periodic boundary conditions were applied in all three directions. The long-range electrostatic interactions are treated using particle-mesh Ewald (PME) method and the van der Waals interactions were calculated using Lennard-Jones potential with a cutoff of 10 Å. After minimization of the system, a short NVT simulation was performed, after which the system was equilibrated at constant temperature (300 K) and constant pressure (1 bar) for 10 ns using Berendsen thermostat and Parrinello–Rahman barostat\textsuperscript{[135]} respectively. Production simulations were then carried out using NPT ensemble simulations with time step of 2 fs. The simulation box was around $\sim 72 \times 72 \times 72$ Å\textsuperscript{3} throughout the simulations.

2.2.2 Characterization

(1) Morphology: The morphology of all the samples was characterized by Scanning Electron Microscopy (SEM) (Quanta 200F) and Optical Microscopy (OM) (Olympus BX51). The film samples were fractured under liquid nitrogen and the fracture surface and free surface were investigated. For optical microscopy observation, the solution samples were directly casted on a glass substrate and dried at 25 °C.

(2) Ionic conductivity: The ambient ionic conductivity was measured via AC impedance spectroscopy (Universal Dielectric Spectrometer BDS 20). The frequency was ranged from 0.1 Hz to $1 \times 10^7$ Hz. A sandwich-like configuration was employed for the testing. The SP solid electrolyte films were placed between two copper electrodes coated by gold with a thickness of 2 mm and 2 cm in diameter. The input testing voltage was 1 V. To measure the ionic conductivity of the samples at different temperatures, the chamber of the Dielectric Spectrometer was placed in an
oven and the temperature was adjusted from 25 to 70 °C. All measurements were repeated at least 3 times for consistency.

(3) Li⁺ transference number: The Li⁺ transference number was measured using Li/electrolyte/Li coin cells where protein solid electrolytes were placed between two lithium metal electrodes. To reduce the interfacial resistance, one droplet of liquid electrolytes (LiPF₆ in EC/DMC, 1 mol/L) was used to wet the surface on both sides of the protein electrolyte. A potentiostatic method combining with AC impedance spectroscopy was performed in electrochemical workstation (CHI 600E) to obtain the values of initial current Iₒ and final steady-state current Iₚ by applying a d.c. polarization voltage of 10 mV. The AC polarization was conducted by applying AC impedance spectroscopy at a frequency from 0.1 Hz to 1M Hz to obtain values of electrode resistance Rₒ and Rₛ. The Li⁺ transference number (tᵢ⁺) was then calculated according to the following equation:

\[
tᵢ⁺ = \frac{Iₚ (U−RₒIₒ)}{Iₒ(U−RₛIₚ)}
\]  

(eqn. 2.1)

(4) Mechanical properties: The moduli of SP solid electrolytes and PEO-based solid electrolytes were characterized by nanoindentation technique (TI950 Hysitron TriboIndenter). The testing samples were prepared by casting the electrolyte solutions directly on metal disks with 15 mm in diameter. For each sample, the modulus was measured at 10 different position and the average value was used to represent the mechanical properties of the samples.
2.3 Results and discussion

2.3.1 Protein denaturation and solubility for lithium salt

The primary matrix material in our solid electrolyte is denatured soy proteins (d-SP) from soybean. It has been reported that soy protein (SP) contains nearly all types of amino acids (Table 2.1). In aqueous environment, the SP is kept at a compact native state with several levels of structures through H-bonding, salt-bridges and hydrophobic interactions. To effectively exploit the interactions from the amino acids on side chains, the SP needs to be denatured. In our experiments, the acetic acid/water mixture and heat (95 °C) are utilized to disrupt those interactions and break the protein native structures. As illustrated in Figure 2.1, a semi-transparent yellow SP solution, i.e. the well-denatured SP is obtained.

Table 2.1 Amino acid profile of soy protein (adapted from Archer Daniels Midland Co.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Amino Acids</th>
<th>g/100g protein</th>
<th>No.</th>
<th>Amino Acids</th>
<th>g/100g protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Glumatic acid</td>
<td>19.2</td>
<td>10</td>
<td>Isoleucine</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>Aspartic Acid</td>
<td>11.5</td>
<td>11</td>
<td>Alanine</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>Leucine</td>
<td>8</td>
<td>12</td>
<td>Glycine</td>
<td>4.1</td>
</tr>
<tr>
<td>4</td>
<td>Arginine</td>
<td>7.7</td>
<td>13</td>
<td>Tyrosine</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>Lysine</td>
<td>6.3</td>
<td>14</td>
<td>Threonine</td>
<td>3.7</td>
</tr>
<tr>
<td>6</td>
<td>Serine</td>
<td>5.3</td>
<td>15</td>
<td>Histidine</td>
<td>2.7</td>
</tr>
<tr>
<td>7</td>
<td>Proline</td>
<td>5.2</td>
<td>16</td>
<td>Tryptophan</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>Phenylalanine</td>
<td>5.2</td>
<td>17</td>
<td>Methionine</td>
<td>1.3</td>
</tr>
<tr>
<td>9</td>
<td>Valine</td>
<td>4.8</td>
<td>18</td>
<td>Cystine</td>
<td>1.3</td>
</tr>
</tbody>
</table>
The denaturation effect is further investigated through the characterization of the SP particle sizes (see SEM and TEM images in Figure 2.2 (a) and (b)). Because of denaturation, the particle size is significantly reduced from ca. 50 μm to ca. 30 nm as estimated by dynamic light scattering shown in Figure 2.2 (c). After the denaturation, certain amount of Li salt (LiClO₄ in this study) is added into the solution creating a protein-ion complex. Finally, the protein-based solid electrolyte is obtained by properly tuning the evaporation temperature and salt concentration. It is noted that solid electrolyte made from pure SP is quite brittle because of the high rigidity of the protein chains, therefore a small amount of high molecular weight poly(ethylene oxide) (PEO) (15 wt%) is added to make the solid electrolyte more flexible and easier to process.

![Figure 2.2](image)

**Figure 2.2.** Morphology and particle size distribution of original and denatured SP. (a) SEM image of the original SP particles. (b) SEM and TEM (the inset) images of SP after denaturation in acetic acid-water solution at 95 °C for 1 hr. (c) Particle size distribution of d-SP measured by dynamic light scattering.

The basic prerequisite for an electrolyte is the ability to dissolve Li salt. The solubility of Li salt in SP is first investigated by dissolving varying loadings of salt, such as 20, 30 and 35 wt% in the SP solution and removing all the solvents at 25 °C. The optical microscopy images are shown in Figure 2.3. As can be seen, at room temperature needle-like LiClO₄ crystals can be
observed once the concentration of LiClO₄ is over 30%, This indicates that 30 wt% is about the maximum solubility of LiClO₄ in SP. This solubility is comparative with conventional polymer electrolytes such as PEO.[52]

![Figure 2.3](image.png)

**Figure 2.3.** Solubility of LiClO₄ in SP at room temperature. (a) – (c) Optical Microscopy images of SP solid electrolytes with varying concentrations of LiClO₄: (a) 20 wt%, (b) 30 wt% and (c) 35 wt%. (d) Schematic illustration of crystallization of LiClO₄ due to saturation of the salt.
2.3.2 Electrochemical and mechanical properties

![Graphs showing ionic conductivity vs. frequency for different loadings of Li salt and evaporation temperatures.]

**Figure 2.4.** Ion-conductivity of SP solid electrolytes with different loadings of Li salt and evaporation temperatures. (a) – (e) Room temperature AC ionic conductivity of SP solid electrolytes with (a) 0 wt%, (b) 20 wt%, (c) 25 wt%, (d) 30 wt% and (e) 35 wt% of LiClO₄ prepared at different evaporation temperatures.

The ionic conductivity of the SP solid electrolytes is highly sensitive to the loading of Li salt and the evaporation temperature during drying process (protein-ion complex formation temperature) in **Figure 2.4.** As shown in **Figure 2.4 (a),** an extremely low ionic conductivity of ~$10^{-11}$ S/cm, possibly comes from the salts dissolved in the original soy protein, is observed for the samples without lithium salt. The ionic conductivity is independent of the evaporation temperatures and the film is brittle. The ionic conductivity is increased with the increasing loading of Li salt. Specifically, 30 wt% loading of Li salt results in the highest ionic conductivity and 35
wt% salt loading slightly reduces the ionic conductivity due to the oversaturation of lithium salt as indicated in Figure 2.3. It is surprisingly found that the evaporation temperature significantly affects the ionic conductivity. As shown in Figure 2.4 (d), there is a three orders of magnitude improvement in ionic conductivity when elevating the evaporation temperature from 25 °C to 40 ~ 60 °C. To clarify how the evaporation temperature contributes to the ionic conductivity, a summary of all the samples in terms of the loading of Li salt and evaporation temperature is shown in Figure 2.5. As illustrated in Figure 2.5 (a), by simply controlling the protein/Li salt ratio and the evaporation temperature, the protein undergoes a significant structural reorganization creating specific pathways for ionic conduction. As shown in Figure 2.5 (b), for the SP solid electrolyte with 30 wt% loading of Li salt, simply increasing the complex formation temperature from 25 °C to 40 °C can significantly improve the ionic conductivity by four orders of magnitude from ~ 10^{-9} to 10^{-5} S/cm. Meanwhile the SP solid electrolyte shows excellent mechanical flexibility as demonstrated by the inset of Figure 2.5 (b).
Figure 2.5. Ionic conductivity of protein-based solid electrolytes at room temperature. (a) Schematic of the control of a protein-ion complex by adjusting protein/ion ratio and complex formation temperature. (b) AC ionic conductivity of SP solid electrolytes with 30 wt% of LiClO$_4$ prepared at different complex formation temperatures (Inset shows that the SP solid electrolyte is mechanically flexible). (c) The effects of complex formation temperature and Li salt loading on the ionic conductivity.

Figure 2.5 (c) summarizes the effects of temperature and Li salt loading on the room temperature ionic conductivity. As shown, the protein-ion complex formation temperature plays a critical role in the ionic conductivity. Increasing the evaporation temperature from 25 °C to 40 °C significantly improves the ionic conductivity, and this effect becomes stronger with the increasing Li salt loading up to 30 wt%. It is noted that this effect on ionic conductivity saturates at a certain
evaporation temperature (ca. 40 °C) and Li salt loading (30 wt%). A further increase of the temperature to 50 or 60 °C, or salt loading to be above 30 wt% (e.g. 35 wt%) does not further improve or even deteriorate the performance, which is probably due to the saturation of Li salt in the protein matrix. The ionic conductivity of the SP solid electrolytes is adjustable in a wide range from $10^{-12}$ to $10^{-5}$ S/cm through simply controlling the evaporation temperature and Li salt loading. Here the SP solid electrolyte sample with 30 wt% loading of Li salt (around the maximum solubility of LiClO$_4$ in SP) and evaporated at 40 °C exhibits the highest ionic conductivity of $\sim 10^{-5}$ S/cm at room temperature. This value reaches the maximum level that has been realized in PEO-based solid electrolytes, including the ones with pure PEO and the ones modified with various nanoparticles.$^{[52][136]}$
The samples with 30 wt% of Li salt and evaporated at 40 °C have been investigated further for electrochemical and mechanical properties. **Figure 2.6 (a)** shows the Arrhenius plot of temperature-dependent conductivities ($\sigma(T)$) from 25 to 70 °C. The data for sample with 30 wt%
of Li salt and evaporated at 25 °C are also included for comparison. In both cases log $\sigma$ is linearly dependent on $1/T$ indicating that there is no phase transition over the temperature range. The conductivity is exponentially dependent on temperature as: $\sigma(T) = \sigma_0 \exp(-E_a/RT)$, in which $\sigma_0$ is the pre-exponential factor and $E_a$ is the activation energy. By fitting the data in Figure 2.6 (a) we can calculate the activation energies for both cases. As shown, the activation energy for SP solid electrolytes evaporated at 40 °C (0.22 eV or 21.2 kJ/mol) is significantly lower than the case with 25 °C (0.36 eV or 34.7 kJ/mol). This value is even close to ceramic superionic conductors, e.g. 0.18-0.22 eV\textsuperscript{[137,138]}. The Li$^+$ transference number is determined by d.c. polarization method. The Nyquist plot and chronoamperometry curve of Li/Conductor/Li cell before and after d.c. polarization are shown in Figure 2.6 (b). The value of Li$^+$ transference number is 0.94 ± 0.03 which is significantly higher than that of conventional PEO-based solid conductors (usually less than 0.4) as compared in Figure 2.6 (c). A similar transference number (0.95-0.98) has recently been obtained in a gelatin protein based solid electrolyte\textsuperscript{[81]}. The high transference number indicates that the ionic transport in SP solid electrolyte is predominated by Li ions. In addition, we also measure the modulus of the sample. As shown, the modulus of the SP solid electrolyte evaporated at both 40 and 25 °C is 1 ± 0.016 GPa. This modulus value is about two orders of magnitude higher than that of the conventional PEO-based solid electrolytes, which is around 0.02 GPa as shown in Figure 2.6 (c). The advantage in mechanical properties for the SP solid electrolyte as compared with conventional PEO-based electrolyte is contributed by two main factors. (1) The difference in flexibility for the polymer chain. It is well known that PEO is a type of flexible polymer due to the C-O bonds in the backbones. However, SP is a type of rigid polymer because of the peptide bonds. (2) The difference in molecular interactions (cohesion). PEO shows simple interchain interactions, while SP processes complicated and strong interactions among different
chains. Due to these two reasons, the modulus that is related to the flexibility and cohesion of the chains for the SP solid electrolyte is much higher than PEO-based systems. If one compares this value with that of ceramic electrolytes (usually in the range of 10 to 100 GPa\textsuperscript{[139,140]}), our SP solid electrolyte actually fills a significant gap between conventional polymeric and ceramic electrolytes in terms of mechanical properties.

### 2.3.3 Mechanism studies

![Figure 2.7](image.png)

**Figure 2.7.** (a) Crystal structure of the 7S homotrimer formed by three α' subunits. The purple portion representing the whole 7S is simulated in our simulations. (b) Simulation box of acetic acid-water solution containing SPI (purple), acetic acid molecules (green) and water molecules (red).

To explore the detailed molecular interactions and investigate the ionic transport mechanism, a series of all-atom molecular dynamics (MD) simulations have been performed. SP is a mixture of proteins containing 2S, 7S, 11S and 15S. Among them, the 7S (or β-conglycinin) is one of the main soy protein components.\textsuperscript{[141,142]} The crystal structure of a 7S homotrimer formed by three α' subunits (PDB ID 1UIK) is shown in **Figure 2.7 (a)**. Due to the computational limitation and structural similarity, we only simulate a portion of 7S as indicated by purple color,
which is composed of a core barrel domain formed by β-sheets and an extended loop domain containing several α-helices. The simulation system containing the protein, water, acetic acid and lithium salts, is illustrated in Figure 2.7 (b).

Figure 2.7. (b) The simulation system containing the protein, water, acetic acid and lithium salts.

Figure 2.8. Denaturation of the soy protein. (a) – (b) Time evolution of the root mean square deviation (RMSD) (a) and the radius of gyration ($R_g$) (b) at three different conditions. (c) The Ribbon representations of the protein structure at different conditions.

Simulations are first performed to study the denaturation process of the soy protein under different conditions. Three cases are created according to the experiments: water at 95 °C, acetic acid-water solution at room temperature and acetic acid-water solution at 95 °C, to show the effects from temperature and acetic acids. The ratio of acetic acid and water molecules is adjusted according to the experimental conditions. The time evolutions of the root mean square deviation (RMSD) and the radius of gyration ($R_g$) of the protein during 200 ns simulations for all three cases has been studied (see Figure 2.8). As clearly shown in Figure 2.8 (a) and (b), the soy protein structure is quite stable at a compact state (small RMSD and $R_g$ values) in water at 95 °C. In acetic-water solution, the formation of hydrogen bonds between acetic acid molecules and soy protein causes the disruption of the protein secondary structures (α-helices and β-sheets) and the
expansion of the protein (increasing RMSD and \( R_g \) values). Increasing the temperature to 95 \(^\circ\)C significantly accelerates the disruption process and cause a quick denaturation of the soy protein, resulting in a flexible and mostly random coil structure as illustrated in Figure 2.8 (c).

**Figure 2.9.** Molecular simulations of protein-ion interactions. (a) – (b) Snapshot of the protein-\( \text{ClO}_4^- \) complex at 25 \(^\circ\)C (a) and 50 \(^\circ\)C (b). The \( \text{ClO}_4^- \) ions interacting with the protein are shown
as gold spheres. The amino acids with positively charged side chains (ARG for Arginine and LYS for Lysine) are shown in red color. (c) Schematic illustration of ClO$_4^-$ cluster formation at high temperature. (d) Time evolution of the number of ClO$_4^-$ interacting with the protein ($N_{\text{ClO}_4^-}$) at different temperatures. (e) The distribution of residence time (interaction strength) for ClO$_4^-$ ions interacting with the protein at 25 °C (green color) and ClO$_4^-$ ions in the cluster at 50 °C (red color). Variation of $N_{\text{ClO}_4^-}$ as a function of different evaporation temperature with 30 wt% loading of LiClO$_4$ (f) and as a function of different lithium salt loading at 50 °C (g). The experimental measurements of the ionic conductivities are shown by green circles for comparison purpose.

Protein-salt interactions play crucial roles to the final ionic transport in SP solid electrolytes. To elucidate the salt-protein interactions and the effects of evaporation temperature, 30 wt% of LiClO$_4$ salts are added into the system and the temperature of the system is controlled at 25, 40, 50 and 60 °C, respectively. From our simulations in **Figure 2.9 (a) and (b)**, we observe a clear accumulation of ClO$_4^-$ anions around the protein surface in all cases. Careful inspection of the simulations indicates that it is due to the strong electrostatic interactions between positively charged residues (Lysine and Arginine as indicated in red color) on the side chain and ClO$_4^-$ ions. At 25 °C, we observe a rather scattered distribution of the ClO$_4^-$ ions. Interestingly as the temperature is increased, the promoted protein random motion and strong ion-protein interactions cause a clear clustering of ClO$_4^-$ ions and protein reorganization as illustrated in **Figure 2.9 (b) and (c)**. The clustering of ClO$_4^-$ ions causes an increase of the number of ClO$_4^-$ interacting with the protein ($N_{\text{ClO}_4^-}$) (**Figure 2.9 (d)**) and further strengthens the ionic interaction as manifested by residence time distribution in **Figure 2.9 (e)**. As shown, the mean residence time for ions in the cluster is one order of magnitude longer than the ions on protein without cluster. **Figure 2.9 (f)**
shows the averaged $N_{\text{ClO}_4}$ at different temperatures. The averaged $N_{\text{ClO}_4}$ first increases with temperature but then saturates above 50 °C. The trend is qualitatively consistent with the experimental measurements of temperature effect on the ionic conductivity as shown in Figure 2.9 (f). Moreover, we also study the effect of salt concentration by controlling salt weight percentage to 10, 20, 30, 40 and 50% while keeping the temperature at 50 °C. As shown in Figure 2.9 (g), the averaged $N_{\text{ClO}_4}$ first increases and then saturates above 30 wt%, which is also consistent with the experimental measurement of the salt concentration effect on ionic conductivities.

![Figure 2.10](image)

**Figure 2.10.** (a) – (e) SEM images of free surfaces (upper) and fracture surfaces (lower) of SP solid electrolytes with an evaporation temperature of 25 °C with LiClO$_4$ loadings of (a) 0 wt%, (b) 20 wt%, (c) 25 wt%, (d) 30 wt% and (e) 35 wt%.
Figure 2.10 shows the SEM images of both free surfaces and fracture surfaces of the SP solid electrolytes with varying LiClO$_4$ loading, which are evaporated at 25 °C. It clearly shows that defects and SP agglomerates are present in all samples. At the same time, even obvious cracks can be found in the free surfaces for 20 and 25 wt% LiClO$_4$ loading cases. When the loading of LiClO$_4$ is higher than 30 wt%, e.g. 35 wt%, salt crystals can be observed in Figure 2.10 (e), which is caused by excessive LiClO$_4$ loading. The defects and protein agglomerates in the electrolyte samples are one of the reasons for the poor ionic conductivity.

![Figure 2.10](image)

Figure 2.11. (a) – (e) SEM images of free surfaces (upper) and fracture surfaces (lower) of SP solid electrolytes with an evaporation temperature of 40 °C with LiClO$_4$ loadings of (a) 0 wt%, (b) 20 wt%, (c) 25 wt%, (d) 30 wt% and (e) 35 wt%.

When elevating the evaporation temperature to 40 °C, the morphologies of the SP solid electrolytes are significantly changed. As can be seen in Figure 2.11, with sufficient LiClO$_4$
loadings such as 30 and 35 wt%, the samples exhibit smooth surfaces without noticeable cracks or SP agglomerates as indicated by Figure 2.11 (b) and (e). The morphological studies indicate that LiClO₄ loading and evaporation temperature are two critical factors affecting the morphologies and the interactions between protein and ions. A good protein-ion interaction that leads to more flexible protein chains helps to form homogeneous protein-ion complex structures and prevent the agglomeration of protein particles.

Both the experiments and simulation results indicate that there exists an optimal evaporation temperature and Li salt loading, over which NClO₄ and the ionic conductivity saturate. Since the attraction of the d-SP to the ClO₄⁻ ions come from specific side groups (Lysine and Arginine), the maximum number of ClO₄⁻ ions attached to the protein must be limited from the number of those groups contained in the protein. The morphology results above also indicate that Li salt loading and evaporation temperature both control the aggregation process of the denatured protein, which finally determines the morphology. For temperature effect, certain amount of heat promotes the flexibility of the protein and facilitates the formation of the cluster of ClO₄⁻ ions. Once the clusters are formed, further increasing the temperature will enhance the kinetic energy of the ClO₄⁻ ions in the cluster and reduce their residence time. Therefore, one must be careful in tuning the amount of salt added and the evaporation temperature for an optimized SP solid electrolyte.

In protein-Li salt solution, the ClO₄⁻ ions are attracted to the protein chain by the positively charged side groups. At a low loading of Li salt (e.g. lower than 20 wt%) and low evaporation temperature (lower than 40 °C), as shown in Figure 2.12 (a), the ClO₄⁻ ions are weakly bonded to the protein surface with a scattered distribution. During the evaporation, it is likely that the strong
protein-protein interactions can cause the segregation of proteins and the ClO$_4^-$ ions, leading to the formation of protein particles and non-uniform ionic distribution as illustrated in Figure 2.12 (a). This is consistent with the SEM image of the fracture surface of the sample as shown, in which one can observe numerous grain boundaries and voids that can hinder the ionic transport. While, with high salt loading and at high evaporation temperature, as shown in Figure 2.12 (b), the ClO$_4^-$ ions on protein surface tends to form clusters due to the elevated flexibility of the protein. The formation of the clusters increases the number of the ClO$_4^-$ ions attached on the protein, and more importantly, significantly strengthens the ion-protein interactions (shown in Figure 2.9) and stabilizes the protein-ion complex. Presumably in this situation the ion-protein interactions are strong enough such that the ClO$_4^-$ ions are tightly locked inside the protein during the evaporation process, which eventually leads to a much smoother morphology and more uniform ionic distribution within the solid electrolyte as confirmed by the SEM image and schematic in Figure 2.12 (b).
**Figure 2.12.** Decoupled ion transport mechanism. (a) At low salt loading and low evaporation temperature, ClO$_4^-$ ions are weakly attached to protein with scattered distribution. Removing of solvents during evaporation causes the segregation of protein and anions, leading to morphology with grain boundaries and voids. (b) At high salt loading and high evaporation temperature, ClO$_4^-$ ions are clustered and strongly locked within the protein and form a highly ion-conductive protein-ions complex. During evaporation, the anions remain in the protein leading to a smooth morphology (SEM image) and uniform anion distribution. (c) Schematic illustration of the decoupled Li$^+$-transportation process. The hopping of Li ions is facilitated by the anions which are strongly locked by the protein through positively charged side chains. The scale bars in SEM images are 1 μm.
Based on the experimental findings and simulation results, we propose a decoupled ionic transport mechanism in SP solid electrolyte. As illustrated by Figure 2.12 (c), the ClO₄⁻ ions are immobile and strongly locked within the protein by specific side groups with positive charges. The migration of Li ions in such system is realized through the hopping among coordination sites (most likely formed by the protein backbone oxygen atoms) and the “locked” anions, a mechanism similar to the conduction in a ceramic electrolyte[36] but completely different from the traditional PEO-based solid electrolytes. The hopping of Li ions is facilitated by the ClO₄⁻ ions that connect those coordination sites; therefore, the ionic transport is decoupled with the protein chain motion. Based on this picture, the ionic conductivity can be improved by increasing the number and/or the spatial arrangement of ClO₄⁻ ions without sacrificing the mechanical properties as demonstrated in our experiments. In addition, the clustering of the anions locally modifies the energy landscape and effectively lowers the activation energy for Li⁺-transport. Finally, since the ClO₄⁻ ions are immobilized by the protein, the ion transport in SP solid electrolytes is dominated by the Li ions leading to a high transference number as shown by the experiments.

2.4 Conclusions

In this study, we successfully fabricate a high-performance protein-based solid electrolyte with superior properties in ionic conductivity, modulus and Li⁺ transference number. Significantly, molecular simulation results indicate that the ion transport in the protein solid electrolyte is facilitated by the anions “locked” by specific functional groups in the protein structure. A decoupled transport mechanism, similar to the conduction in ceramic conductors, is proposed to explain all findings in experiments. This work opens up a new avenue for exploiting biomaterials for fabricating advanced solid electrolytes with a unique ion-transport mechanism.
CHAPTER 3

COMPOSITE ELECTROLYTES WITH FAST ION-CONDUCTION BY

MANIPULATING PROTEIN CONFIGURATION

3.1 Introduction

Energy storage devices (ESDs) such as lithium ion batteries (LIBs) assembled with liquid electrolytes (LEs) have gained significant success in commercial applications over the past decades.\textsuperscript{52} With the rapid development of electric vehicles, flexible and wearable electronic devices, there is an increasing demand on advanced ESDs which show excellent safety and mechanical flexibility, in addition to high energy/power densities. Is is well known that, the widely used LEs are the main reason for safety concerns of LIBs due to their flammability and leakage issues, which represents the most critical issue for current LIBs technology.\textsuperscript{143,144} Replacing the LEs by solid electrolytes, such as solid polymer electrolytes (SPEs) or inorganic ceramic electrolytes, is believed the most attractive solution to resolve the safety issues\textsuperscript{40,145}. Among the two types of solid electrolytes, SPEs are very attractive owing to their excellent mechanical flexibility and also materials processability, which cannot be realized in inorganic solid electrolytes. As a result, considerable attention has been paid to fabricating SPEs by dissolving lithium salts (e.g., LiClO\textsubscript{4}, LiPF\textsubscript{6}, LiTFSI, etc.) in different kinds of polymer hosts, such as poly(ethylene oxide) (PEO)\textsuperscript{54,66}, polyacrylonitrile (PAN)\textsuperscript{50,51}, poly(propylene carbonate)\textsuperscript{146,147} and so on. However, these simple salt-polymer solid solution systems always give rise to an extremely low ionic conductivity well below $10^{-5}$ S/cm at room temperature\textsuperscript{52,148} which blocks
them from practical applications. Therefore, improving the ion-conductivity of SPEs to be on the level for practical application (e.g. $10^{-4}$ S/cm at room temperature) is the key task for the development of SPEs.

To improve the ionic conductivity, different strategies have been reported in previous studies. Addition of plasticizer is the first common strategy. The plasticizer usually include liquid electrolytes with high ionic conductivity or low molecular weight polymers, which can significantly improve the mobility of polymer chains and so the ionic conductivity.\textsuperscript{[56,57]} However, unfortunately, this strategy requires a high loading of plasticizer to achieve an ionic conductivity around the liquid electrolyte level, which, most of the time, destroys the attractive advantages of SPEs, such as good mechanical properties and safety. Efforts to achieve a good balance between ion-conductivity and mechanical properties have been the main focus for the studies on this type of solid polymer electrolytes, also well-known as gel-type polymer electrolytes.\textsuperscript{[149,150]} Different from the first strategy, addition of functional fillers represents another attractive method to improve the ion-conductivity without sacrificing mechanical properties. It is generally believed that the introduction of nanofillers into SPEs, e.g. ceramic nanofillers, can effectively improve the ionic conductivity primarily due to two different mechanisms. The first one is the reduction of crystallinity of the polymer host by the effects of nanofillers.\textsuperscript{[151,152]} The second one is the possible fast ion-conduction at the filler-polymer interfaces, which is contributed by Lewis acid-base interactions between the ions and the ceramics surface.\textsuperscript{[153,154]} Some of the ceramic nanofillers, including MgO\textsuperscript{,\cite{155}} Al\textsubscript{2}O\textsubscript{3}\textsuperscript{,\cite{44,63,64}} SiO\textsubscript{2}\textsuperscript{,\cite{70,153,156}} TiO\textsubscript{2}\textsuperscript{,\cite{65,66,157}} etc. have been found very effective to increase the ionic conductivity of SPEs. However, for these nanofillers, due to agglomeration caused by weak polymer-ceramic interaction and non-conductive nature of the nanofillers, further improvement remains a big challenge.\textsuperscript{[153,158]} Therefore, efforts on solid
composite polymer electrolytes (CPEs) have been focused on modifying the traditional nanofillers or developing new nanofillers for improved ion-conductivity.

Surface modification of the nanofillers represents a simple but significant approach. It can improve not only the dispersion quality of the nanofillers, but also enables the control of interfaces and interactions among the polymer host and ions. To realize fast ion-conduction, the surface functionalization is usually aimed to achieve appropriate interactions between the nanofiller surface and ions, which can facilitate the ion-dissociation and improve the ionic conductivity. For example, it is found that core-shell silica with boron moiety on the shell by Shim and Lee et al.\cite{72}, and TiO$_2$ grafted-PEGMEM/SMA nanohybrid by Ma and Wei et al.\cite{159} can extensively enhance the ionic conductivity of the CPEs. Design of new nanofillers with special morphology or ion-conductive properties is another attractive method to build fast pathways for ion-transport, such as the mesoporous silica by Kim and Park et al.\cite{160}; metal-organic frames (MOFs) by Yuan and Liu et al.\cite{154}. Among these new nanofillers, ion-conductive nanofillers, such as Li$_3$N\cite{151}, Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$\cite{161}, are very effective as they can provide additional conduction pathways and mechanisms for fast ion-conduction. In particular, one-dimensional (1-D) ion-conductive nanofillers have been reported as advanced nanofillers for solid CPEs.\cite{162,163} 1-D ion-conductive nanofillers can help to build fast ion-conduction pathways through the interface or the ion-conductive filler itself. Therefore, it is believed that the design of advanced nanofillers with unique surface structures and properties for fast ion-conduction is a primary and promising method for the fabrication of high-performance composite solid polymer electrolytes.

In our previous work, we have demonstrated that denatured soy-protein can form unique protein-ion complex and finally result in a solid ion-conductor, that is, a protein ion-conductor, showing ionic conductivity at the level of $10^{-5}$ S/cm at room temperature.\cite{164} At the same time,
proteins have been well studied as effective surfactant for dispersing nanoparticles in polymer matrix to exhibit good interfacial properties.\textsuperscript{[165,166]} Based on these previous studies, in this study, we further developed a new hybrid nanofiller via combining the ion-conductive soy-protein and one classic ceramic nanoparticle, TiO\textsubscript{2}, to form a unique protein-ceramic hybrid nanofiller for improving the ion-conductivity of solid polymer electrolytes. The matrix of the solid polymer electrolyte is an amorphous material based on the complex of ultrahigh molecular weight poly(ethylene oxide) (UHMWPEO) and LiClO\textsubscript{4}.\textsuperscript{[167,168]} Through experiments and molecular simulations, here we demonstrate that possible fast ion-conductive pathways may be constructed by proper adjusting the structure of the soy-protein attached onto the TiO\textsubscript{2} nanoparticles. In addition, we found that, for the resultant composite solid polymer electrolytes, the mechanical properties, electrochemical stability, as well as adhesion properties are significantly improved by the unique protein-ceramic hybrid nanofillers.

3.2 Experimental

3.2.1 Electrolyte preparation

The hybrid nanofillers were prepared via two procedures in this work. For preparation of TiO\textsubscript{2}-(SP-open) hybrid, 6 wt\% TiO\textsubscript{2} dispersion was prepared by dispersing certain amount of rutile TiO\textsubscript{2} powders (Sigma Aldrich) in 5 mL acetic acid aqueous solvent with a pH value of 2. The dispersion was treated in an ultrasonic bath for 3 min and was then stirred at 95 °C for 10 min until the temperature was stable. Afterwards, a varying loading of soy protein isolate powders (Archer Daniels Midland Co.) according to weight ratios of TiO\textsubscript{2}/soy protein (SP) (e.g., 9:1, 8:2, 7:3, 6:4, 5:5) was added into the dispersion and stirred for another 1 hr. The as-prepared solution was cooled down to room temperature and then was treated by ultrasonifier (Branson 250) with an amplitude.
of 15% for 3 min in an ice bath to allow uniform adsorption of protein on the surface of TiO$_2$ nanoparticles. For TiO$_2$-(SP-close) hybrid, 3 wt% of soy protein isolate powders were first denatured in the same acetic acid aqueous solvent at 95 °C for 1 hr to form yellowish solution. The denatured SP solution was cooled down to room temperature, after which rutile TiO$_2$ powders were added into the denatured SP solution according to the same weight ratios as that for TiO$_2$-(SP-open) hybrid. The TiO$_2$ nanoparticles were dispersed with aid of ultrasonifier with an amplitude of 15% for 3 min in an ice bath. At the same time, a 1.6 wt% PEO solution was prepared by dissolving PEO powders (Mw=5,000,000 g/mol, Sigma Aldrich) in DI water. A certain amount of LiClO$_4$ (Sigma Aldrich) was added into the PEO solution based on a molar ratio of O/Li as 6:1. To fabricate PEO composite electrolytes, the as-prepared TiO$_2$-SP mixture solution was added into the PEO solution, and the mixture was then stirred vigorously for 20 min at room temperature to ensure homogeneity. Afterwards, the mixture solution was casted onto unsticky paper as substrate by a film applicator to control the thickness. After removing all the solvents at room temperature, the solid film was further dried in a vacuum oven at 60 °C for 12 hr and the resulting films can be carefully delaminated from the substrate. The thickness of all the samples was measured by a digital micrometer with a typical thickness of 55 ± 4 µm.

### 3.2.2 Molecular simulations

All MD simulations were carried out using GROMACS package 5.0.5\textsuperscript{[169]} with GROMOS 53A6 force field. The SPC model was chosen for water molecules and parameters of acetic acid force field were adopted from Radola et al.\textsuperscript{[170]} Three chlorine ions were added to neutralize the system. The long-range Coulomb interactions were treated with the PME method, while the van der Waals (vdW) interactions were handled using Lennard-Jones potential with a cutoff of 1.4 nm.
Periodic boundary conditions were applied in all three directions. All simulation systems were prepared and visualized using PACKMOL\textsuperscript{[171]} and VMD\textsuperscript{[172]}, respectively. Due to the computational limitation and structure similarity of soy protein, we only simulate a portion of a 7S homotrimer (PDB ID: 1U1K) in our system (see Refs. for details\textsuperscript{[164,166]}). In this study, (110) rutile surface of TiO\textsubscript{2} was selected to represent TiO\textsubscript{2} nanoparticles because of its stability compared with other surfaces. We constructed the perfect TiO\textsubscript{2} (110) rutile surface by duplication of small unit cells with the lattice parameters of a = 2.95812Å and c = 4.59373Å. The charges and Lennard-Jones parameters for rutile surface were taken from Luan \textit{et al.} For each simulation, after minimization of the system, a short NVT simulation was performed, after which the system was equilibrated at constant temperature and constant pressure for 10 ns using Berendsen thermostat and Parrinello-Rahman barostat\textsuperscript{[135]}. To study the effect of TiO\textsubscript{2} on denaturation of the protein, two different simulation conditions including denaturing protein w/ and w/o TiO\textsubscript{2} nanoparticles in acetic acid solution were conducted according to experiments. Simulations are run for 200 ns at 368 K and three independent realizations in each condition were performed for statistical consistency. Once the denaturation processes completed, interactions between denatured SP and TiO\textsubscript{2} plate via the above two methods were studied at 300 K and carried out for additional 200 ns for each case.

\textbf{3.2.3 Characterization}

(1) Morphological studies: The morphology of all the samples was examined by Scanning Electron Microscopy (SEM) (Quanta 200F) and Optical Microscopy (OM) (Olympus BX51). The film samples were fractured under liquid nitrogen and the facture surfaces were investigated. For optical microscopy observation, the solution samples were directly casted on a glass substrate and
were dried at room temperature. The agglomerate size distribution of the samples was analyzed by ImageJ based on SEM images and more than 150 agglomerates were counted.

(2) Ionic conductivity: The ambient ionic conductivity was measured via AC impedance spectroscopy (Universal Dielectric Spectrometer BDS 20). The frequency was ranged from 1 Hz to $1 \times 10^7$ Hz. The CPE films were sandwiched between two stainless steels in argon-filled glove box to assemble symmetric SS/SPE/SS cells. To measure the ionic conductivity of the samples at different temperatures, the chamber of the Dielectric Spectrometer was placed in an oven and the temperature was adjusted from 25 to 90 °C. All measurements were repeated at least 3 times for consistency.

(3) Electrochemical stability: For electrochemical stability measurement, Li/SPE/SS cells were assembled. Linear cyclic voltammetry with a scan rate of 10 mV/s was applied at a potential window of 0 to 6 V by using an electrochemical workstation (CHI 600E).

(4) Cell assembly and electrochemical characterization: For all-solid-state half-cell assembly, CPEs were sandwiched between Li metal anodes and LiCoO$_2$ cathodes and assembled into coin-cells in an argon-filled glovebox. To prepare LiCoO$_2$ cathodes, LiCoO$_2$ electrode powders (MTI) were mixed with carbon black (Super C45, MTI) and PEO (Mw=600,000 g/mol, Sigma Aldrich) electrolyte solution in acetonitrile according to a weight ratio of 6 : 3 : 1 to form a uniform slurry. The slurry was cast onto aluminum foil by a Doctor blade and was dried in vacuum oven for 12 h at 60 °C to be transferred to the glovebox. The typical loading of active materials was around 1.2 mg/cm$^2$. The electrochemical performance of the half-cells was examined by cycling the cells between 3 and 4.2 V by using a battery analyzer (BST8-MA, MTI) at 65 °C.
(5) Adhesion property: The adhesion force of samples was determined by Atomic Force Microscopy (AFM, Bruker) at room temperature. Spring constant of the cantilever (Bruker AFM Probes, Madison, WI) was calibrated by thermal noise method.

3.3 Results and discussion

3.3.1 Strategy for manipulating protein configuration

Figure 3.1. Schematic for the preparation of TiO$_2$-soy protein hybrid nanofillers with different protein configuration and ion-conductive properties: (a) Conventional TiO$_2$-soy protein hybrid with insufficient and weak attachment of denatured soy protein chains onto TiO$_2$ surface. (b) Ion-conductive TiO$_2$-soy protein hybrid with unique surface coating of soy protein chains forming special ion-channel. The solvent employed for these two procedures is a mixture of acetic acid (AA) and DI-water with a weight ratio of 8:2.
To prepare the protein-ceramic hybrid nanofillers, we proposed two different procedures as shown in Figure 3.1. The soy proteins (SPs) in aqueous environments at native state are compact with several levels of structures through various inter-chain bonding and interactions, such as H-bonding, salt-bridges, hydrophobic interactions and disulfide bonding. In order to open the structures of protein and expose the functional groups, denaturation of SP at different conditions was first studied. As shown in Figure 3.1 (a), in our first procedure, the soy protein was first denatured at high temperature (95 °C) in acidic environment (aq. acetic acid, pH=2) for 1 h. Then, the TiO$_2$ nanoparticles were added into the solution and dispersed through ultrasonication. In this case, the denatured soy protein works simply as a surfactant to TiO$_2$ particles. In the second procedure as shown in Figure 3.1 (b), the TiO$_2$ nanoparticles were first pre-dispersed in acidic environment (aq. acetic acid, pH=2), then the SP was added and denatured together with the TiO$_2$ nanoparticles at 95 °C in the same acidic solvent for 1 h. In this situation, the TiO$_2$ nanoparticles actively participate in the protein denaturation process. The rutile surface of TiO$_2$ is polar due to the negative charge on oxygen atoms and positive charge on the Ti atoms. Moreover, on the surface the Ti atoms may even be hydroxylated and the oxygen atoms may be protonated to certain degree depending under certain experimental conditions. Therefore, the presence of the TiO$_2$ nanoparticle may significantly affect the protein denaturation environment, leading to more open and flexible protein structures as illustrated in Figure 3.1 (b). We expect that the promoted denaturation of the protein and exposure of the protein functional groups will greatly impact the interactions as well as protein configurations, and eventually lead to CPEs with much improved electrochemical, mechanical and adhesive properties.
3.3.2 Morphological, electrochemical and mechanical properties

Figure 3.2. Morphological studies of the TiO$_2$ nanoparticles, TiO$_2$-SP hybrids and the resultant composite polymer electrolytes (CPEs). (a) – (c) SEM images of untreated TiO$_2$, TiO$_2$-(SP-close) and TiO$_2$-(SP-open) hybrids, respectively. (d) – (f) SEM images of the CPEs with 5 wt% loading of untreated TiO$_2$, TiO$_2$-(SP-close) and TiO$_2$-(SP-open) hybrids, respectively. (g) – (i) Distribution of agglomerate size for the CPEs loaded with (g) untreated TiO$_2$, (h) TiO$_2$-(SP-close) hybrid and (i) TiO$_2$-(SP-open) hybrid.
For CPEs, the dispersion of the nanofillers is a critical factor affecting the ion-conduction pathways and the mechanical properties. The dispersion of different nanofillers in the suspension is first examined by SEM and the results are shown in Figures 3.2 (a) – (c). From these SEM images, significant differences in dispersion between the hybrid nanofillers and the untreated TiO\textsubscript{2} nanoparticles are observed. For the untreated TiO\textsubscript{2}, the nanoparticles tend to severely aggregate (Figure 3.2 (a)) and form agglomerates; however, as shown in Figures 3.2 (b) and (e), the two types of TiO\textsubscript{2}-SP hybrids both exhibit significantly reduced particle size, indicating a much-improved dispersion in the suspension. Similar results have been found for the resultant CPEs as shown in Figures 3.2 (d) – (e). In specific, one can find a poor dispersion of the untreated TiO\textsubscript{2} in the electrolyte matrix (the PEO-based solid polymer electrolyte with LiClO\textsubscript{4} loading of 28 wt%). The size of the agglomerates as shown in Figure 3.2 (d) is about 1 µm (see Figure 3.2 (g)). In contrast, for the CPEs with the two types of hybrid nanofillers, the dispersion of the hybrid nanofillers in the matrix is greatly improved with much reduced agglomerate size of 500 ~ 600 nm in average as shown in Figures 3.2 (e) and (f) (also see the size distribution in Figure 3.2 (h) and (i)). These results indicate that the protein treatment on the TiO\textsubscript{2} surface plays an important role in improving the dispersion quality and enhancing the compatibility between the nanoparticle and polymer host, which will significantly affect the ionic transport as will be discussed later.
In addition, to evaluate the thermal stability of the hybrid nanofillers and prove the presence of protein on the TiO$_2$ surface, thermogravimetric analysis (TGA) was performed and the results are shown in Figure 3.3. As shown, the TiO$_2$-(SP-open) hybrid nanofiller shows a dramatic weight loss from ca. 250 °C due to degradation of protein. At the same time, the TGA data indicate that there is about 12 wt% protein coated onto the TiO$_2$ surface.

**Figure 3.3.** TGA curves of TiO$_2$-(SP-open) hybrid nanofiller as compared with untreated TiO$_2$. 
Figure 3.4. (a) Comparison of room temperature ionic conductivity for pure PEO-LiClO$_4$ electrolyte, CPEs with 5 wt% loading of untreated TiO$_2$, TiO$_2$-(SP-close) hybrid and TiO$_2$-(SP-open) hybrid nanofillers with weight ratio TiO$_2$/SP of 4:1. (b) Ionic conductivity of CPEs with the two types of hybrid nanofillers at varying loadings (weight ratio of TiO$_2$: SP = 4:1).

The electrochemical and mechanical properties of the CPEs with two types of TiO$_2$-SP hybrids were further studied and compared with the pure SPE (i.e., the matrix of the CPEs without nanofillers) and CPE with untreated TiO$_2$. We measured the ionic conductivity and modulus of the CPEs and the results are shown in Figure 3.4. As shown in Figure 3.4 (a), the ionic conductivities for all three types of CPEs are much higher than that of the pure PEO-LiClO$_4$ electrolyte which is around $5 \times 10^{-6}$ S/cm at room temperature. More importantly, the two hybrid nanofillers exhibit significant improvement in the ionic conductivity as compared with the CPE with untreated TiO$_2$ nanoparticles. In specific, the CPE loaded with 5 wt% TiO$_2$-(SP-open) hybrid nanofiller yields the highest ionic conductivity of $6 \times 10^{-5}$ S/cm at room temperature, which is about one magnitude higher than that of the pure PEO-LiClO$_4$ electrolyte, and 5 times of the CPEs with TiO$_2$-(SP-close) hybrid or untreated TiO$_2$ nanofillers. To identify the optimum loading, the loading of the two hybrid nanofillers was varied from 1 to 10 wt% and the ion-conductivity results of these CPEs are shown in Figure 3.4 (b). As shown, the ionic conductivity of the CPEs with TiO$_2$-(SP-open) hybrid is evidently higher than that of CPEs with TiO$_2$-(SP-close) hybrid throughout all the loading range, and the maximum ionic conductivity is reached at 5 wt% loading. The ionic conductivity for both cases decreases slightly when the loading exceeds 6 wt% possibly due to formation of agglomerates as shown in Figure 3.5. One finds that with high loadings of TiO$_2$-(SP-close) hybrid, such as 8 and 10 wt%, the agglomerate size greatly improves to 0.9 and 1.2 µm, respectively.
Figure 3.5. (a) – (d) SEM images of CPEs with 1, 3, 8 and 10 wt% loading of TiO$_2$-(SP-open) hybrid, respectively; (e) – (h) SEM images at higher magnification corresponding to (a) – (d), respectively; (i) – (l) Distribution of agglomerate size of CPEs with 1, 3, 8 and 10 wt% loading of TiO$_2$-(SP-open) hybrid nanofillers, respectively.

We further investigate the effect of the weight ratio between the SP and TiO$_2$ on the ionic conductivity. As shown in Figure 3.6 (a), the ionic conductivity is optimized at $6.5 \times 10^{-5}$ S/cm by the TiO$_2$-(SP-open) hybrid with TiO$_2$/SP ratio of 4:1. It indicates that the TiO$_2$/SP ratio for the hybrids plays an important role in affecting both dispersion and ionic conductivity (see SEM images in Figure 3.6 (b) – (e)). The above results reveal that the TiO$_2$-(SP-open) hybrid is more effective for improving the ionic conductivity as compared with conventional TiO$_2$-(SP-close) hybrid. Based on the above findings, we can conclude that the unique TiO$_2$-SP hybrid (TiO$_2$-(SP-}
open) hybrid), when prepared by the modified procedure as shown in Figure 3.1 (b) at appropriate TiO$_2$/SP ratio, can assist in building special ion-conduction pathways for fast ion-conduction in the resultant CPEs. The possible mechanisms will be further discussed in our simulation studies later.
Figure 3.6. (a) The effect of protein percentage in the TiO$_2$-(SP-open) hybrid on ionic conductivity (loading of the hybrid nanofiller: 5 wt%). (b) – (e) SEM images of CPEs with varying loading of protein in the TiO$_2$-(SP-open) hybrid nanoparticles: 10, 30, 40 and 50 wt%, respectively.

In addition to ionic conductivity, mechanical property is another critical property for solid electrolytes. A high modulus and good mechanical flexibility is highly desired for SPEs and CPEs to be used as separator and suppress the growth of lithium dendrites.\textsuperscript{[118,175]} Figure 3.7 (a) shows the mechanical properties of all the CPEs with 5 wt% loading of nanofillers as compared with pure PEO-LiClO$_4$ electrolyte. The moduli of all the CPEs are much higher than pure PEO-LiClO$_4$ electrolyte, and the CPE with TiO$_2$-(SP-open) hybrid nanofiller yields the highest modulus of ca. 1 MPa at 1 Hz. There are two important points worthy of discussion here. First, the moduli of CPEs with the two kinds of TiO$_2$-SP hybrid nanofillers are significantly higher than that of the CPE with untreated TiO$_2$ nanoparticles. Second, the modulus for the CPE with TiO$_2$-(SP-open) hybrid is slightly higher than that of the CPE with conventional TiO$_2$-(SP-close) hybrid, which may indicate that the interface between TiO$_2$-(SP-open) hybrid and PEO-LiClO$_4$ matrix is much better than that for the CPE with conventional TiO$_2$-(SP-close) hybrid. Figure 3.7 (b) summarizes both the ionic conductivities and moduli of all CPEs. It is well known that there is always a trade-off between ion-conductivity and modulus in SPEs or CPEs due to the coupling effects between the ion-conduction and chain mobility of the matrix.\textsuperscript{[53,145,164]} However, for the CPEs with TiO$_2$-(SP-close) hybrid and TiO$_2$-(SP-open) hybrid, they show simultaneous improvement in both ionic conductivity and modulus as shown in Figure 3.7 (b). In particular, the CPE loaded with TiO$_2$-(SP-open) hybrid shows the highest ionic conductivity and modulus among all the CPEs. We believe that the unique protein/TiO$_2$ and protein/PEO-LiClO$_4$ interactions in the TiO$_2$-(SP-open) hybrid CPE play critical roles in these properties.
Figure 3.7. (a) Storage modulus of pure PEO-LiClO$_4$ electrolyte and CPEs with 5 wt% loading of untreated TiO$_2$, TiO$_2$-(SP-close) hybrid and TiO$_2$-(SP-open) hybrid. (b) Summary of ionic conductivity and mechanical properties of the CPEs as compared with the pure SPEs.

The ionic conductivity of the CPEs as a function of temperature is further studied and displayed in Figure 3.8 (a). The ionic conductivity of the CPEs with TiO$_2$-(SP-open) hybrid is found to be the highest throughout the temperature range. In specific, the ionic conductivity for the CPE with conventional TiO$_2$-(SP-close) hybrid or the pure PEO-LiClO$_4$ electrolyte is in the range of $10^{-5} - 10^{-4}$ S/cm when the temperature varies from 20 to 90 °C. However, for the CPE with TiO$_2$-(SP-open) hybrid, the ion-conductivity increases to ca. $7 \times 10^{-4}$ S/cm at 90 °C, which is close to the level of liquid electrolytes. In addition to ionic conductivity, the contribution of the nanofillers to the electrochemical stability is also characterized and the results are shown in Figure 3.8 (b). It is known that a wide electrochemical stability of the electrolytes is crucial for safety. As shown the pure PEO-LiClO$_4$ electrolyte is electrochemically stable below ca. 5.1 V, which is higher than that of organic liquid electrolytes (4.5 V)$^{[31,176]}$. More importantly, for the two CPEs with TiO$_2$-SP hybrid nanofillers, the electrochemical stability is evidently improved (5.2 V for TiO$_2$-(SP-close)-CPE and 5.4 V for TiO$_2$-(SP-open)-CPE). This result indicates that the addition
of TiO$_2$-SP hybrid can suppress the decomposition of PEO-LiClO$_4$ electrolyte, which is consistent with other studies on nanofillers.[71,177,178]

To further investigate the electrochemical performance of the CPEs in a real device, the half cells containing the CPE with TiO$_2$-(SP-open) hybrid nanofillers were assembled and tested at 65 °C. Figure 3.8 (c) presents the charge-discharge profiles for LiCoO$_2$/CPE-TiO$_2$-(SP-open)-hybrid/Li half cells at varying C-rates. As shown, typical LiCoO$_2$ voltage profiles can be observed for the half cells, which suggests that the cells work very well and stably. Figure 3.8 (d) displays the discharge capacity and Coulombic efficiency versus cycle number at 0.1 C. Specifically, one can find that the capacity slightly decreased from 135 to 128 mAh/g after 24 cycles, and the Coulombic efficiency is slightly lower (about 95%) than traditional LCO system. This result indicates two points: firstly, it means that the new electrolyte can work simultaneously as separator and ion-conductor as designed; secondly, it means that there are some complicated factors contributing to the battery performance, such as, possible instable microstructures of the electrode, and the unknown SEI layer between the new solid electrolyte and Li metal.
Figure 3.8. (a) Arrhenius plots of ionic conductivity of CPEs with the TiO$_2$-SP hybrid nanofillers as compared with pure PEO-LiClO$_4$ electrolyte. (b) Electrochemical stability studies of the CPEs as compared with pure PEO-LiClO$_4$ electrolyte. (c) Discharge-charge profiles of LiCoO$_2$/CPE-TiO$_2$-(SP-open) hybrid/Li cells with varying C-rates tested at 65 °C. (d) Cycle performance and coulombic efficiency of LiCoO$_2$/CPE-TiO$_2$-(SP-open) hybrid/Li cells at 0.1 C tested at 65 °C.
3.3.3 Adhesion properties

**Figure 3.9.** Adhesion properties of the CPEs with TiO$_2$-SP hybrid nanofillers. (a) – (c) Adhesion force mapping by AFM for the CPEs loaded with (b) TiO$_2$ and (c) TiO$_2$-(SP-open) hybrid compared with (a) pure PEO-LiClO$_4$ electrolyte. (d) Comparison of the average adhesion force of the solid electrolytes. (e) Digital photo showing a strong adhesion between the CPE loaded with TiO$_2$-(SP-open) hybrid and stainless steel. (f) Schematic of the possible mechanism for the TiO$_2$-(SP-open) hybrid to improve the adhesion of the CPEs.

For SPEs, a strong adhesion of electrolyte allows stable contact between electrode and electrolyte.$^{[21,128]}$ The adhesion force mappings of the electrolyte systems obtained by peak force QNM characterization via AFM are displayed in **Figures 3.9 (a) – (c).** For pure PEO-LiClO$_4$ electrolyte as shown in **Figure 3.9 (a),** the adhesion force is between 6.9 and 10.5 nN. The force is contributed by the amorphous structures of the PEO-Li$^+$ complex as revealed by our previous
For the CPE with untreated TiO$_2$ nanoparticles, the adhesion force decreases and ranges from 2.1 to 7.9 nN. However, interestingly the TiO$_2$-(SP-open) hybrid can enhance the adhesion force as shown in Figure 3.9 (c), and the adhesion force ranges from 6.8 and 13.9 nN. Figure 3.9 (d) compares the average adhesion force for all these solid electrolyte samples. As shown, the average adhesion force of the CPE loaded with TiO$_2$-(SP-open) hybrid is the highest among all the samples. (~ 11 nN). As demonstrated in Figure 3.9 (e), the CPE filled with TiO$_2$-(SP-open) hybrid exhibits strong adhesion to a stainless steel. At the same time, it shows good mechanical properties (0.9 MPa at 5 HZ) and flexibility allowing stretching without fracture.

Although the mechanisms for adhesion contribution may be complicated, we believe that the SP coating onto the TiO$_2$ nanoparticles is the key for the improved adhesion properties since SP has been widely used as a class of adhesive for engineering applications.$^{[179]}$ To illustrate this contribution, Figure 3.9 (f) lists the possible interactions at the interface contributed by the protein chain. The unique and richness of functional groups along with the protein chain may provide strong interactions to the substrate surface, including charge-charge interactions, hydrogen bonding, Van der Waals force, π-π interactions etc.$^{[118]}$

3.3.4 Simulation studies of the TiO$_2$-SP hybrids

Simulation studies on the soy-protein (SP) denaturation. As illustrated in Figure 3.1, careful control of the denaturation/mixing process may result in quite different protein configurations and protein/particle interactions, and eventually lead to different electrochemical and mechanical properties of the resulting CPEs. To uncover the underlying mechanisms, molecular dynamics (MD) simulations mimicking the experimental conditions have been carried out in this study. Our simulations have been divided into two parts. The first part is to study the
protein denaturation process under two conditions as illustrated in Figure 3.1. In the first case, the SP was denatured in the AA/DI solvent at 95 °C without TiO\(_2\) nanoparticles. As shown by the snapshot in Figure 3.10 (a) and the time evolution of the radius of gyration (R\(_g\)) in Figure 3.10 (c), the protein structure quickly changes during the first 20 ns with a dramatic increase of R\(_g\) from 1.9 nm to 2.1 nm for the SP denatured without TiO\(_2\). Figure 3.10 (a) also reveals that only part of the protein has been unfolded, while the rest still keeps compact throughout the rest of the simulation with a relatively stable R\(_g\) fluctuates around 2.1 nm. Interestingly, for the SP denatured with the TiO\(_2\) nanoparticles, the SP undergoes much more dramatic structural changes. As shown in Figure 3.10 (c), the R\(_g\) of the protein increases from ~1.5 nm to ~2.5 nm during 200 ns simulations, and nearly all of the original structures have been destroyed (see the snapshot in Figure 3.10 (b)).

The results clearly indicate that in the second case, the TiO\(_2\) nanoparticle strongly affect the protein denaturation process. Inspection of the TiO\(_2\) surface indicates a significant accumulation of the solvent molecules, including both acetic acid and water, due to the strong electrostatic interactions. As demonstrated in Figure 3.10 (d) and (e), this surface accumulation causes the depletion of solvent molecules in the bulk. The solvent molecules, such as water, in solution tend to stabilize the original protein structures through H-bonding, therefore a depletion of the water likely promotes the protein denaturation.
Figure 3.10. Molecular simulation studies of the soy-protein (SP) denaturation with or without TiO$_2$. (a) – (b) Snapshot of the final state of denatured SP in mixture solvent of acetic acid (yellow) and H$_2$O (red) under two conditions: w/o and w/ TiO$_2$ (shown as plate), respectively. (c) Time evolution of the radius of gyration ($R_g$) of denatured SP under the two different conditions. (d) Illustration of adsorption of acid molecules on TiO$_2$ surface. (e) Number density of acetic acid (oxygen atom on hydroxyl group) and water (oxygen atom) molecules along the Z direction.

*Simulation studies on the TiO$_2$/SP interactions.* We have demonstrated above that TiO$_2$ plays a critical role in denaturing protein. During the second part of our simulations we focus on the protein-particle interactions after protein denaturation. We first reduced the system temperatures to room temperature, then added TiO$_2$ nanoparticle into the first case and carried out another 200 ns simulations. The initial and final states of protein-TiO$_2$ configurations for both
cases are illustrated in **Figure 3.11**. As shown in **Figure 3.11 (a)**, for the first case a weak absorption of SP by the TiO$_2$ was observed and the denatured SP chain with a more closed configuration jumped back and forth near the TiO$_2$ surface. In contrast, for the second case we found a quite strong SP adsorption onto the nanoparticle surface throughout the 200 ns simulation as shown in **Figure 3.11 (b)**. The denatured SP was locked onto the TiO$_2$ surface throughout the entire process. Analysis of the individual energetic contributions from different residues indicates that the strong adsorption is dominated by the electrostatic interactions between the positively charged amino acids (such as Arg-30 and Arg-38 as illustrated in the inset of **Figure 3.11 (b)**) and the negatively charged oxygen atoms on TiO$_2$ rutile surface. As shown in **Figure 3.11 (b)**, the electrostatic interactions are strong enough such that the Arginine groups are able to penetrate the first solvent layer and direct contact with the rutile surface.

Although it is still difficult to completely explain why the TiO$_2$-(SP-open) hybrid nanofiller can notably outperform other nanofillers (i.e., TiO$_2$-(SP-close) hybrid and untreated TiO$_2$) as found in the experimental studies, the above simulation studies bring critical clues for us to understand the mechanisms. Based on our experimental and simulation results, we propose a possible model as illustrated in **Figure 3.11 (c)** for explaining the unique contribution to ion-conduction in the CPE from the TiO$_2$-(SP-open) hybrid. In this model, the presence of TiO$_2$ promotes the denaturation of SP and the exposure of protein functional groups. As a result, the denatured SPs strongly bind to TiO$_2$ surface and form a stable SP coating. The protein coating on TiO$_2$ surface improves the dispersion of nanofillers in solution, meanwhile the functional groups on protein coating also actively interact with the polymer matrix (PEO in our experiments) leading to improved mechanical strength and flexibility. More importantly, during the fabrication of CPEs, the denatured SP can interact with lithium salts through strong electrostatic interaction between
backbone oxygen of protein and Li$^+$, and form anion clusters via strong electrostatic interactions between positive charge side groups (e.g. Lys. Arg.) of protein and anions (ClO$_4^-$), as revealed by our previous study$^{[164]}$, creating ion conductive pathways and facilitating (see Figure 3.11 (c)) fast Li$^+$-transportation. This model indicates that manipulating the protein configuration by nanofillers will enable us to build novel ion channels for fast ion-conduction in solid polymer electrolytes.

Meanwhile, we also propose a possible model to help us understand how the TiO$_2$-(SP-open) hybrid nanofiller help the ion-transportation inside the CPEs. For the CPE with untreated TiO$_2$ nanoparticles, the contribution from TiO$_2$ to the ion-conduction is limited by the big agglomerates as revealed by SEM images shown in Figure 3.2 (a) – (d). In this situation, the transportation of lithium ions is mainly controlled by the polymer matrix, the TiO$_2$ agglomerates do not help much and may even block the ionic transport.$^{[153,158]}$ On the other hand, protein treatment can significantly reduce the particle aggregation$^{[166]}$. At the same time, the denatured proteins on TiO$_2$-SP hybrid may form unique ionic pathways for ion transport, depending on the protein configuration as revealed in this study. More specifically, even though the TiO$_2$-(SP-close) sample shows similar nanofiller dispersion as that for TiO$_2$-(SP-open) sample (see SEM images in Figure 3.2 (b), (c), (e), (f)), the ion-transport is very different because of the difference in protein configuration structures on the TiO$_2$ surfaces. For the TiO$_2$-(SP-open) nanofillers, the completely unfolded configuration can help form effective ionic pathways to accelerate the ionic conduction,$^{[164]}$ which explains the improved ion-conductivity.
Figure 3.11. Simulation studies on the interactions between denatured SP and TiO$_2$ nanoparticles. (a) Weak and unstable absorption of SP onto TiO$_2$ nanoparticles in TiO$_2$-(SP-close) hybrid. (b) Strong and stable absorption of SP onto TiO$_2$ nanoparticles in TiO$_2$-(SP-open) hybrid. (c) Schematics of fast ion-conduction channel formed in TiO$_2$-(SP-open) hybrid and ion transport pathways in CPEs with TiO$_2$-(SP-open) hybrid compared with TiO$_2$-(SP-close) hybrid.
3.4 Conclusions

This work has revealed a unique biotechnology via manipulating protein structures for constructing fast ion-conduction pathways in SPEs. In specific, it is found that when TiO$_2$ nanoparticles actively participate in protein denaturation, a more open and flexible structures of SP can be obtained. The elevated structural flexibility promotes protein-TiO$_2$ interactions and helps to form fast ion-conduction pathways. Adding such hybrid nanoparticles in SPEs, ionic conductivity, mechanical properties and adhesion properties are notably improved.
CHAPTER 4

COMPOSITE ELECTROLYTES WITH CORE-SHELL PROTEIN@TIO₂

HYBRID NANOWIRES

4.1 Introduction

Among various emerging energy storage devices, lithium-ion batteries (LIBs) have been intensively investigated to satisfy the ever-growing demands for cutting-edge technologies of portable devices, large-scale energy systems, electric vehicles, etc.¹²⁷,¹²⁸ For current LIBs, the expansive use of organic liquid electrolytes, however, poses potential hazards due to their volatility and flammability.¹⁸¹,¹⁸² In this regard, solid-state electrolytes made of polymers or inorganic materials, which feature appropriate mechanical strength and safety to suppress dendrite growth, hold great promise in replacing the liquid electrolytes. Comparing the two categories of solid electrolytes, solid polymer electrolytes (SPEs) possess more design flexibility and easy processability for different battery applications, which make them very appealing candidates for all-solid-state flexible LIBs. To date, tremendous efforts have been made to fabricate SPEs based on various polar polymers, such as poly(ethylene oxide) (PEO)¹⁸³–¹⁸⁵, polyacrylonitrile (PAN)¹⁷¹,¹⁸⁶,¹⁸⁷, polyurethane (PU)¹⁸⁸,¹⁸⁹, polypropylene carbonate (PPC)¹⁹⁰,¹⁹¹, etc. Nonetheless, the broad applications of SPEs are impeded by their low ionic conductivity (10⁻⁸ ~ 10⁻⁶ S/cm) at room temperature.³⁸,¹⁹² To effectively improve the ionic conductivity of SPEs, approaches such as plasticization, block-copolymerization, polymer blending, adding nanofillers, etc. have been shown to be feasible. The aim of these methods is to reduce the crystalline regions of the polymer hosts, since ion-conduction is
commonly believed to be confined in amorphous phase of the polymer hosts\cite{145}, even though the work by Zhang et. al\cite{197} revealed that the crystalline region can transport Li$^+$ as well. As a result, unfortunately, the decreased crystallinity can inevitably deteriorate the mechanical properties of the SPEs. Therefore, to attain good ionic conductivity and mechanical properties is one of the principal challenges for developing high-performance SPEs. Of the aforementioned attempts, it is noted that introducing nanofillers is viewed as a very attractive approach, which can enhance the ionic conductivity and compensate the mechanical properties of the SPEs simultaneously.

In addition to intervening local reorganization of polymer chains to reduce crystallinity, incorporating nanofillers such as ceramic nanofillers into SPEs can promote lithium salt dissociation and thereof Li$^+$ transport via Lewis acid-base interaction at the polymer-nanofiller interfaces.\cite{151,198} Great research efforts have been focused on employing diverse classic ceramic nanofillers such as SiO$_2$\cite{70,180}, TiO$_2$\cite{199,200}, ZrO$_2$\cite{201,202} into SPEs, which were proved to be effective for enhancing the performance of SPEs. However, because of the nonconductive nature of the nanofillers, poor polymer-nanofiller interactions and uncontrolled ion-conduction pathways, the ionic conductivity of the resultant composite polymer electrolytes (CPEs) is still limited in the range of $10^{-6} \sim 10^{-5}$ S/cm at room temperature. In this context, more effectively improving the ionic conductivity still remains critically challenging. Thus, over the past few decades, tremendous endeavors have been devoted to fabricating advanced nanofillers with unique functions or morphologies via modifying classic nanofillers or creating new nanofillers.

Modifying classic nanofillers through rational surface functionalization represents an effective method for achieving fast ion-conduction in SPEs. Surface functionalization can usually improve the polymer-filler compatibility, adjust filler-ion interaction, and thus facilitate ion-conduction. For instance, mesoporous silica-based single-ion conductor\cite{203} and TiO$_2$-PMMA
hybrids\(^{199}\) were demonstrated to significantly enhance the ionic conductivity when they were filled into the polymer hosts. Moreover, design of new nanofillers that show unique interactions with ions is another viable approach to realizing fast ion-conduction. To that end, numerous ion-conductive inorganic nanofillers, such as \(\text{Li}_{6.75}\text{La}_{2}\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}\)\(^{182,204,205}\), \(\text{Li}_{0.3}\text{La}_{0.55}\text{TiO}_{3}\)\(^{206,207}\), \(\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_{4})_{3}\)\(^{208,209}\), etc. have been investigated, which showed the capability of more effectively building fast pathways for ion-conduction owing to their intrinsic ability of migrating \(\text{Li}^+\). Further, in addition to particle-based nanofillers, there were emerged considerable studies on one-dimensional ion-conductive nanofillers that helped build more continuous and efficient pathways for rapidly transporting \(\text{Li}^+\) depending on the polymer-filler interfaces or the nanofillers themselves. For example, \(\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_{3}\) nanowires fabricated by Liu and Cui et al.\(^{71}\), \(\text{Li}_7\text{La}_2\text{Zr}_2\text{O}_{12}\) garnet-type nanowires reported by Yang and Chan et al.\(^{210}\), etc. remarkably enhanced the ionic conductivity of the CPEs as compared with the particle-shaped counterparts. In a nutshell, design of one-dimensional nanofillers with unique surface properties is considered to be one of the most promising strategies for constructing fast ion-conduction pathways for fabricating high-performance CPEs.

In our own work\(^{211}\), we demonstrated a novel biotechnology using soy protein for functionalizing surface properties of classic ceramic nanofiller, \(\text{TiO}_2\) nanoparticles, to enable faster ion-conduction in PEO-based SPEs. The unique soy-protein-treated \(\text{TiO}_2\) hybrid nanoparticles could substantially enhance the ionic conductivity of the SPEs (\(\sim 6 \times 10^{-5}\) S/cm, 25 °C) by one order of magnitude compared to the filler-free ones. This is due to the fact that soy protein was able to conduct \(\text{Li}^+\) and form fast ion-conduction channels on \(\text{TiO}_2\) surface. Interestingly, our exploration indicated that the protein configuration and protein-\(\text{TiO}_2\) interaction played important roles in conducting \(\text{Li}^+\). In particular, the faster ion-conduction pathways could only be realized...
on the basis of specific protein configuration, which could be appropriately tuned by proper protein treatment conditions. In the current work, we report core-shell protein@TiO₂ hybrid nanowires that can more effectively build faster ion-conduction networks in SPEs as compared with protein-TiO₂ hybrid nanoparticles. In addition, the roles of protein on interacting with ions are systematically analyzed. The study reveals that protein can considerably adsorb anions resulting in promoted dissociation of lithium salts and conduction of Li⁺. As a consequence, the CPEs embedded with the core-shell protein@TiO₂ hybrid nanowire present notably enhanced ionic conductivity (~ 1.1 x 10⁻⁴ S/cm, 25 °C), mechanical properties, electrochemical stability and Li⁺ transference number in comparison with the ones with hybrid nanoparticles.

4.2 Experimental

4.2.1 Sample preparation

(1) Preparation of TiO₂ nanowires: TiO₂ nanowires were fabricated via electrospinning of precursor solution that was prepared as follows. Typically, 1.92 mL titanium tetraisopropoxide (Sigma Aldrich) was mixed with 7.2 mL acetic acid/ethanol (1:1 by volume), which was stirred for 1 hour. Meanwhile, 0.54 g polyvinylpyrrolidone (PVP, Sigma Aldrich, Mw = 1,300,000 g/mol) was added to 9 mL ethanol and was stirred for 1 h. These two solutions were mixed together and stirred for another 1 h. The abovementioned procedures were conducted at room temperature. The mixture solution was then transferred to a 20 mL plastic syringe with a stainless needle connecting to 17 kV high-voltage power supply. The electrospinning was carried out by using an electrospinner (Inovenso). The distance between the needle and the plate-type collector covered by aluminum foil was 15 cm. The flow rate for feeding the solution was controlled constant to be
2 ml/h by a digital pump (Inovenso). The obtained fiber mats were calcinated in a muffle furnace at 500 °C for 3 h in air with a ramping rate of 4 °C/min to remove organics.

(2) Fabrication of protein-TiO₂ hybrid nanowires or nanoparticles: The TiO₂ nanowires were first dispersed in acetic acid solution (pH = 2) by ultrasonic bath for 10 min with a concentration of 1.5 wt%. The mixture solution was then heated and stirred in an oil bath at 95 °C for ca. 10 min until the temperature stayed stable. Afterwards, soy protein isolate powders (Mw = 50,000 ~ 100,000 g/mol, Archer Daniels Midland Co.) were added into the heated mixture solution according to a weight ratio of 7 : 3 (TiO₂ : protein), which was stirred for 1 h to denature soy protein. The mixture dispersion was cooled down naturally to room temperature for subsequent experiments. To prepare the protein-TiO₂ hybrid nanoparticles, same procedures were applied except that the anatase TiO₂ nanoparticles (Sigma Aldrich) were used instead of TiO₂ nanowires.

(3) Fabrication of composite polymer electrolytes: The composite polymer electrolytes were prepared by conventional solution-casting technique. Briefly, PEO powers (Mw = 5,000,000 g/mol, Sigma Aldrich) were dissolved in deionized water with a concentration of 1.6 wt%, which was stirred vigorously until homogeneity. LiClO₄ (Sigma Aldrich) was then added to the obtained PEO solution according to a molar ratio of O : Li = 6 : 1. A varying amount of cooled down protein-TiO₂ mixture dispersion was added to above PEO-LiClO₄ solution following loadings of nanofillers: 1, 5, 10 and 15 wt%. Subsequently, the mixture was then stirred for 20 min until homogeneity and was casted on anti-sticky paper as the substrate by a doctor blade. Finally, the composite polymer electrolytes were obtained by further drying in a vacuum oven at 60 °C for 12 hr and transferred to Ar-filled glove box for subsequent experiments. The thickness of all the samples was measured by a digital micrometer with a typical thickness of ca. 70 µm.
4.2.2 Characterization

(1) Morphological, structural and mechanical properties characterization: The morphology of the nanowires was characterized by Scanning Electron Microscopy (SEM) (FEI Quanta 200F) and Transmission Electron Microscopy (TEM) (FEI Technai G2 20 Twin). Element mapping was conducted by using Tescan Vega3 SEM. To confirm the adsorption of Li salt by protein, excessive loading of LiClO$_4$ (50 wt%) was added to the dispersion of protein-TiO$_2$ hybrid nanowires. The solid mixture was rinsed by ethanol for several times to remove unbonded and residual Li salt and then dried at a vacuum oven at 60 °C overnight. EDS mapping was performed on the aforementioned solid mixture to probe the Li salt. Infrared spectra were recorded by using a Fourier transform infrared spectrophotometer (FTIR) (Nicolet iS10). The crystalline structure of the nanowire specimens was examined by X-ray Diffraction (XRD) (Rigaku Miniflex 600) using Cu K$_\alpha$ radiation over a range of 10 ~ 60°. Differential Scanning Calorimetry (DSC) analysis was conducted using a Mettler Toledo DSC in a nitrogen atmosphere with a heating rate of 10 °C/min. The weight of the samples was controlled to be 5 ~ 6 mg. The weight percentage of protein in the hybrid nanowires was investigated by Thermogravimetric Analysis (TGA) (TA Instruments) in nitrogen atmosphere at a heating rate of 10 °C/min. The mechanical properties of the composite electrolytes were investigated by using a Rheometer (TA Instruments) via frequency sweep over a range of 0.1 – 100 Hz at room temperature.

(2) Electrochemical characterization: To measure the ionic conductivity, the CPE films were sandwiched between two stainless steels (SS) in Ar-filled glove box to assemble symmetric SS/CPE/SS configuration. The ionic conductivity was measured via AC impedance spectroscopy (Universal Dielectric Spectrometer BDS 20) over a frequency range of $1 \sim 10^7$ Hz. For electrochemical stability measurement, Li/CPE/SS cells were assembled in glove box. Linear
cyclic voltammetry with a scan rate of 3 mV/s was applied at a potential window of 0 to 6 V using an electrochemical workstation (CHI 600E). Li\(^+\) transference number was measured by chronoamperometry method with a polarization voltage of 10 mV on Li/CPE/Li cells. The Li\(^+\) transference number (t\(^+\)) was calculated via eqn. 4.1:

\[
t^+ = \frac{I_{ss} (U-R_oI_o)}{I_o (U-R_{ss}I_{ss})}
\]

where U refers to the polarization potential; I\(_o\) and I\(_{ss}\) refers to the initial current and steady-state current respectively; R\(_o\) and R\(_{ss}\) refers to the electrode resistance before and after polarization respectively. To assemble solid-state half cells, the electrodes were prepared by mixing 60 wt% LiCoO\(_2\), 20 wt% carbon black (SuperC45, MTI) and 20 wt% PEO solid electrolyte (Mw = 600,000 g/mol, O : Li = 6 : 1) by bowl-mill until homogeneity. The slurry was casted on carbon-coated aluminum foil by a doctor blade and was subsequently dried in a vacuum oven at 60 °C for 12 h. The loading of active materials was controlled to be 3.2 ~ 3.3 mg. The cells were examined at a cut-off voltage of 3 – 4.2 V by using a battery analyzer (BST8-MA, MTI) at 65 °C. For Li/CPE/Li symmetric cells, in first 5 cycles, 0.3 mAh/cm\(^2\) of Li metal was deposited at a current density of 0.1 mA/cm\(^2\) to stabilize the cells. Subsequently, in each cycle 0.5 mAh/cm\(^2\) of Li metal was deposited at various current density of 0.2 and 0.5 mA/cm\(^2\). The measurement was carried out at 65 °C.

4.3 Results and discussion

4.3.1 Design strategy

As illustrated in Figure 4.1 (a), the pristine soy protein (SP) is compact with several levels of structures bonded by strong interchain interactions, e.g. hydrogen-bonding, ionic-bonding,
disulfide-bonding, etc. In our previous work we explored that TiO$_2$ nanoparticles (NPs) could greatly assist in opening up the structures of SP, which resulted in a very flexible protein configuration. Notably, we demonstrated that via proper manipulation of SP structures, SP could form unique ion-conduction channels on TiO$_2$ surface for promoting Li$^+$ transport. This was realized on grounds that the participation of TiO$_2$ in protein denaturation process dramatically changed the protein structures, which destroyed original protein structures and unfolded the protein chains to more sufficiently expose its functional groups. The functional groups of protein might have unique interactions with the lithium salts to help dissociation and transportation of ions. As a result, the advanced SP-TiO$_2$ nanofillers with fast ion-conduction channels on the surface by protein gave rise to remarkably improved ionic conductivity. More detailed explanation can be found in our previous studies. In the present work, we fabricate core-shell structured SP@TiO$_2$ nanowires (NWs) that can more effectively build faster ion-conduction pathways owing to their ion-conductive surface by protein-functionalization and one-dimensional morphology that is conducive to form continuous pathways to longer distance. As shown in Figure 1b, the TiO$_2$ NWs were fabricated by electrospinning of polyvinylpyrrolidone (PVP) polymer fibers containing relevant precursor and then calcinated at 500 °C in air for 3 h. The SP@TiO$_2$ core-shell NWs were realized via in-situ growth of SP layer on TiO$_2$ NWs in TiO$_2$-engaged protein denaturation at 95 °C in acetic acid solution (pH = 2) for 1 h. In this protein-functionalization process, protein was stably coated on the surface of TiO$_2$ NWs due to strong electrostatic interactions, which will be discussed later in morphology studies. The comparison of the possible ion-conduction pathways for the CPEs filled with NP-/NW-shaped nanofillers is illustrated in Figure 4.1 (b). It is anticipated that the embedded core-shell SP@TiO$_2$ hybrid NWs can lead to more continuous conductive pathways of longer distance along the protein-functionalized polymer-nanofiller interfaces, as
compared with segregated SP-TiO$_2$ NPs. Consequently, with the better networked-structure of nanofillers, the ionic conductivity and mechanical properties of the NW-filled CPEs can be substantially enhanced.

**Figure 4.1.** (a) Schematic of fabricating advanced protein-ceramic hybrid nanofillers via building protein ion-conduction channels on TiO$_2$ surface. (b) Fabrication of core-shell protein@TiO$_2$ NWs via protein-functionalization on TiO$_2$ NWs and the advantages of protein@TiO$_2$ NWs over protein-TiO$_2$ NPs for building faster ion-conduction pathways in SPEs.
4.3.2 Morphology of protein@TiO₂ nanowires

**Figure 4.2.** FTIR spectra of as-spun nanofibers as compared with calcinated TiO₂ NWs. (a) – (b) FTIR spectra of as-spun PVP-TiO₂ composite nanofibers and TiO₂ NWs, respectively. (a) – (c) EDS mapping of TiO₂ NWs showing the distribution of Ti and O elements.

**Figure 4.2** shows the FTIR spectra of TiO₂ NWs as compared with PVP/TiO₂ composite fibers. As shown in **Figure 4.2 (a)**, PVP/TiO₂ composite fibers show typical peaks such as C-N (1288 cm⁻¹) and C=O (1666 cm⁻¹). After the composite fibers experienced calcination, these characteristic peaks disappear and only a broad peak in the range of 500 – 700 cm⁻¹ can be observed and assigned to the Ti-O-Ti bonding[213,214]. Meanwhile, the Energy-dispersive X-ray spectroscopy (EDS) mapping of TiO₂ NWs only exhibit signals from Ti and O elements as shown in **Figure 4.2**.
These results suggest that the calcination of PVP/TiO$_2$ composite fibers completely remove all polymers and other organics, and TiO$_2$ NWs are successfully fabricated.

**Figure 4.3.** (a) – (b) SEM and TEM images of TiO$_2$ NWs and core-shell SP@TiO$_2$ NWs, respectively. The insets are the statistics of fiber diameter. (c) EDS mapping of Ti, O, C, N and S elements in core-shell SP@TiO$_2$ NWs.

The SEM and TEM images in **Figure 4.3 (a)** indicate that the TiO$_2$ NWs with a high aspect ratio and smooth surface show particle-accumulated structure. After treated by protein, the average diameter of the TiO$_2$ NWs increases from 221 nm to 246 nm (see the insets in **Figure 4.3 (a) and (b)**), which is due to the growth of protein coating on the surface of TiO$_2$ NWs. This result can be confirmed by TEM images of the SP@TiO$_2$ NWs in **Figure 4.3 (b)**. As is shown, a very thin layer of protein (ca. 8 nm) can be observed on the surface of TiO$_2$ NWs leading to a core-shell structure,
in which the protein layer is the shell and the TiO$_2$ NW is the core. Meanwhile, the core-shell SP@TiO$_2$ NWs exhibit similar morphological feature of pristine TiO$_2$ NWs, indicating a high aspect ratio that is beneficial for building continuous ion-conduction networks. Moreover, the EDS mapping of SP@TiO$_2$ NWs is also compared with the pristine TiO$_2$ NWs to probe the presence of protein. Figure 4.3 (c) displays the EDS mapping of SP@TiO$_2$ NWs. It clearly shows that in addition to Ti and O elements owing to TiO$_2$ NWs, C, N and S elements (S element is scarcely distributed due to its slight content in protein) are distributed on the TiO$_2$ NWs, which are attributed to the presence of protein on the TiO$_2$ surface. All the above results prove that protein is coated on the surface of TiO$_2$ NWs, which eventually turns out unique core-shell SP@TiO$_2$ NWs.

Figure 4.4. (a) XRD patterns of SP, TiO$_2$ NWs and SP@TiO$_2$ NWs. (b) FTIR spectra of SP, TiO$_2$ NWs and SP@TiO$_2$ NWs. (c) Schematic illustration of possible interactions between SP and TiO$_2$.

The crystalline structures of the NWs were inspected by X-ray diffraction (XRD) and the results are shown in Figure 4.4 (a). It evidently identifies the amorphous nature of SP, which shows a broad peak of 20 in the range of 15 ~ 25°. At the same time, the XRD pattern of TiO$_2$ NWs calcinated at 500 °C reveals six peaks at 25.3, 37.9, 48.1, 53.9 and 55.2°, which can be indexed to (101), (004), (200), (105) and (211) plans of anatase phase, respectively. This is
consistent with previously reported studies\textsuperscript{[217,218]}. For the core-shell SP@TiO\textsubscript{2} NWs, a superimposition XRD pattern of SP and TiO\textsubscript{2} can be observed, which indicates an integration of two compositions. In specific, the peak intensity of the crystalline phase of TiO\textsubscript{2} distinctly decreases; it is contributed by the presence of amorphous protein coating on the surface of TiO\textsubscript{2} NWs. To reveal the interactions between SP and TiO\textsubscript{2} NWs, FTIR spectra were recorded and the results are displayed in Figure 4.4 (b). One finds that the FTIR spectrum of SP shows several characteristic peaks at 1238, 1394, 1528 and 1661 cm\textsuperscript{-1} corresponding to amide III (N-H stretching), amide III (C-N stretching), amide II (N-H bending) and amide I (C=O stretching), respectively.\textsuperscript{[219,220]} For native TiO\textsubscript{2} NWs, the broad peak in the range of 500 ~ 700 cm\textsuperscript{-1} can be assigned to the Ti-O-Ti bonding\textsuperscript{[213,214]} However, in regard to the core-shell SP@TiO\textsubscript{2} NWs, the peak of N-H stretching (amide III) at 1238 cm\textsuperscript{-1} almost disappears, indicating that there might be strong interactions between -NH groups of protein and TiO\textsubscript{2} NWs. It is worth noting that in acidic environment when pH value is below the isoelectric point (PI) of specific amino acid, the amino acid will be positively charged. In this work, SP was denatured together with TiO\textsubscript{2} NWs in acetic acid solution with a very low pH value of 2. Therefore, due to their protonated amine side groups, all amino acids have an overall positive charge in solution state (all amino acids have PIs above 2.77).\textsuperscript{[221]} Similarly, even in solid-state after removing all solvents, when the pH value increases to neutral form, several amino acids still carry a net positive charge, such as Lysine (PI=9.87), Arginine (PI=10.76) and Histidine (PI=7.59). As a result, the positively charged side groups can strongly interact with negatively charged oxygen atoms of TiO\textsubscript{2} via ionic interaction as depicted in Figure 4.4 (c). This strong adsorption eventually drives the in-situ growth of protein layer on the TiO\textsubscript{2} surface and a stable core-shell SP@TiO\textsubscript{2} composite structure.
4.3.3 Electrolyte properties

Figure 4.5. (a) SEM images of CPEs with 10 wt% loading of various nanofillers: SP-TiO$_2$ NPs, TiO$_2$ NWs and SP@TiO$_2$ NWs. (b) Differential scanning calorimetry (DSC) curves of various CPEs loaded with 10 wt% nanofillers compared with pure PEO and PEO electrolyte.

The dispersion of nanofillers in the polymer host significantly impacts the formation of ionic conduction pathways and mechanical properties of the resulting CPEs. The microstructures of various CPEs loaded with different nanofillers were investigated by SEM as shown in Figure 4.5 (a). It can be seen that the CPE with SP-TiO$_2$ NPs exhibit a great number of agglomerates of NPs due to their extremely high surface energy, despite that SP can enhance the compatibility of the NPs with polymers due to its rich functional groups. Hence the increased particle-particle junctions might hinder the conduction of Li$^+$. In contrast, for both TiO$_2$ NWs and core-shell SP@TiO$_2$ NWs cases, they demonstrate random distribution of high-aspect-ratio NWs without notable aggregation, which results in much fewer cross-junctions. This is beneficial for constructing longer and more continuous conduction pathways for Li$^+$ along the interfaces between the polymer and NWs. Furthermore, as crystallinity of the CPEs plays an important role in their ionic conductivity, we examined the crystallinity of various CPEs as compared with pure ultrahigh-molecular-weight PEO (UHMWPEO) that was used as the polymer matrix in this work.
As shown in Figure 4.5 (b), pure UHMWPEO is a semi-crystalline polymer, displaying a distinct melting peak at ca. 68 °C. However, when loaded with sufficient amount of LiClO₄, e.g. 28 wt% in this study, the melting peak completely disappears indicating that the crystallization of UHMWPEO is greatly suppressed due to significant polymer chain entanglement and strong interaction between oxygen atoms of UHMWPEO and Li⁺, which yields amorphous UHMWPEO-Li⁺ complex. The amorphous UHMWPEO-Li⁺ complex as the electrolyte host can generate several desired properties, including high ionic conductivity, good adhesion and so forth as revealed by Wang et al.[167] In terms of the CPEs with various nanofillers (10 wt% loading), the melting peak of UHMWPEO is absent likewise. Therefore, it is evident that the introduction of various nanofillers has no significant impact on the crystallinity of the CPEs, which all show amorphous structures.

**Figure 4.6.** (a) Ionic conductivity of CPEs with 10 wt% loading of various nanofillers compared with PEO electrolyte. (b) Summary on ionic conductivity of CPEs with various nanofillers versus loading of nanofillers. (c) Dependence of ionic conductivity of CPEs with 10 wt% loading of various nanofillers on temperature.

As shown in Figure 4.6 (a), the three types of CPEs present much higher ionic conductivity than that of PEO electrolyte (ca. 5 x 10⁻⁶ S/cm). It is noted that as compared to the CPE with SP-
TiO$_2$ NPs, the ones with NWs (both TiO$_2$ NWs and SP@TiO$_2$ NWs) as the nanofillers show further improvement in the ionic conductivity, which implies that NWs can build faster pathways for conducting Li$^+$ than NPs do. More importantly, one finds that the CPE with core-shell SP@TiO$_2$ NWs shows the highest ionic conductivity of $1.1 \times 10^{-4}$ S/cm, which is significantly higher than the case of TiO$_2$ NWs ($5.6 \times 10^{-5}$ S/cm). To optimize the loading of nanofillers, a series of loading varied from 1 to 15 wt% was investigated and the results are shown in Figure 4.6 (b). Of all the CPEs with various nanofillers, the ionic conductivity of the CPE with SP@TiO$_2$ NWs is the highest throughout all loading ranges, and the maximum ionic conductivity can be reached at a nanofiller loading of 10 wt%. When further increasing the loading of SP@TiO$_2$ NWs, the ionic conductivity drops slightly due to the increased NW aggregates possibly. In addition, it can be found that the CPE with SP-TiO$_2$ NPs shows the lowest ionic conductivity over all loading ranges, except for the 5 wt% case showing a higher ionic conductivity than that of the CPE with TiO$_2$ NWs. At the same time, the ionic conductivity sharply drops when the loading of SP-TiO$_2$ NPs exceeds 5 wt%. This possibly results from the severe aggregation of SP-TiO$_2$ NPs that intervenes the ion-conduction by the increased cross-junctions.

The above results indicate two points worthy of discussion. Firstly, the one-dimensional NWs can more effectively build fast ion-conduction pathways than NPs, due to the better dispersion of NWs forming fewer cross-junctions and longer pathways. In addition, the one-dimensional NWs with a high aspect-ratio is conducive to building continuous conduction networked-structure as compared with zero-dimensional NPs that are easily segregated and form more cross-junctions impeding the ion-conduction. This gives rise to significantly higher ionic conductivity for the CPEs loaded with TiO$_2$ NWs or SP@TiO$_2$ NWs as compared with the CPE with SP-TiO$_2$ NPs. Secondly, on the basis of two types of NW-filled CPEs, core-shell SP@TiO$_2$
NWs evidently further enhance the ionic conductivity. This indicates that the protein as the shell of the hybrid NWs can greatly assist the ion-conduction at the polymer-nanofiller interface owing to its unique interaction with ions as will be discussed later. Even though the ion-conduction is contributed by many complicated factors, e.g. the crystallographic structure of the TiO\textsubscript{2} nanofillers that might affect the interaction with ions and the resulting protein structure, the dimensional morphology is a very critical element accounting for the further improvement in ionic conductivity of the CPEs.

The temperature-dependence of the ionic conductivity is displayed in Figure 4.6 (c). As shown in this figure, the enhancement of ionic conductivity can be observed for all electrolyte specimens with increased temperature. The slope of the ionic conductivity against temperature does not significantly change, implying a very slight phase transition of the polymer matrix, which is contributed by the highly-amorphous structure of PEO. In specific, the ionic conductivity of the CPE with SP@TiO\textsubscript{2} NWs is found to be the highest throughout all the tested temperature range. For the filler-free SPE and the CPEs with SP-TiO\textsubscript{2} NPs and TiO\textsubscript{2} NWs, the ionic conductivity increases in the range of $10^{-6} \sim 10^{-4}$ S/cm when elevating the temperature from 25 to 80 °C. Notably, the ionic conductivity of the CPE with SP@TiO\textsubscript{2} NWs reaches about $2 \times 10^{-3}$ S/cm at 80 °C, which is at the same level of liquid electrolytes.
Figure 4.7. Mechanical properties of CPEs with various nanofillers. (a) Storage modulus of various CPEs with 10 wt% loading of nanofillers as compared with pure PEO electrolyte. (b) Summary of storage modulus of various CPEs versus loading of nanofillers. (c) Relationship between ionic conductivity and storage modulus of various CPEs as compared with pure PEO electrolyte.

The storage moduli of the CPEs were measured by frequency sweep at room temperature and are compared with filler-free PEO electrolyte as shown in Figure 4.7 (a). It is found that as compared with pure PEO electrolyte, the three types of CPEs show significantly higher storage modulus. Importantly, the CPE with 10 wt% SP@TiO$_2$ NWs presents the highest storage modulus among all CPEs. Figure 4.7 (b) depicts the storage modulus of CPEs with SP@TiO$_2$ NWs, SP-TiO$_2$ NPs and TiO$_2$ NWs at 1 Hz as a function of the filler loading. It is observed that the modulus increases with an increase in the filler loading, and the CPE with SP@TiO$_2$ NWs reveals the highest modulus throughout all loading range while the TiO$_2$ NW case stays in the middle. On the basis of abovementioned results, we can conclude that the one-dimensional NWs can more significantly enhance the mechanical properties due to the continuous networked-structure formed by the NWs as compared with isolated zero-dimensional NPs. More importantly, in light of the fact that the CPE with SP@TiO$_2$ NWs exhibits much higher modulus than that of the CPE with TiO$_2$ NWs, it is believed that the protein layer on the surface of TiO$_2$ NWs plays an important role in improving the interfacial compatibility between polymer matrix and nanofillers. This is because protein obtains numerous polar/nonpolar functional groups derived from abundant amino acid groups, which makes protein act as an effective surfactant or “connective bridge” between the polymer matrix and nanofillers.$^{[165]}$
Figure 4.7 (c) demonstrates the summarized relationship between ionic conductivity and storage modulus of various CPEs. For comparison, pure PEO electrolyte is also included in this figure. It is known that there is always a trade-off between ionic conductivity and modulus because the ion-transport is coupled with segment mobility of the polymer host.\cite{53,164} As shown in Figure 4.7 (c), however, ionic conductivity and modulus can be simultaneously improved by addition of SP-TiO$_2$ hybrid nanofillers (SP-TiO$_2$ NPs and SP@TiO$_2$ NWs) or TiO$_2$ NWs. Particularly, the CPE with SP@TiO$_2$ NWs shows the highest ionic conductivity and modulus of the three types of CPEs. This indicates that protein plays an important role in promoting ionic conductivity and mechanical properties, which can contribute to build faster ion-conduction pathways and enhance the interface between the nanofillers and polymer hosts.

Figure 4.8. Electrochemical properties of CPEs with various nanofillers. (a) Linear sweep voltammetry (LSV) curves of CPEs with various nanofillers as compared with pure PEO electrolyte measured at 3 mV/s. (b) Evolution of current with time during polarization of
Li/CPE/Li configuration at a voltage of 10 mV; the inset is the impedance spectra before and after polarization. (c) Summary on Li$^+$ transference number of CPEs as compared with pure PEO electrolyte. (d) EDS mapping of SP@TiO$_2$ NWs adsorbing LiClO$_4$. Loading of nanofillers in all CPEs: 10 wt%.

To investigate the stability of the CPEs against high voltage, the electrochemical stability window was measured, and the results are shown in Figure 4.8 (a). As shown, the electrochemical stability window of three types of CPEs is broader than that of pure PEO electrolyte (ca. 5.0 V). In specific, the CPE with 10 wt% SP@TiO$_2$ NWs presents the highest electrochemical stability up to ca. 5.3 V, as compared with the cases of TiO$_2$ NWs (ca. 5.1 V) and SP-TiO$_2$ NPs (ca. 5.2 V). This indicates that the employment of core-shell SP@TiO$_2$ NWs is conducive to expand the electrochemical stability window.

Moreover, we surprisingly found that SP@TiO$_2$ NWs can effectively improve the Li$^+$ transference number of the CPEs. Figure 4.8 (b) shows the chronoamperometry results of the CPE containing 10 wt% SP@TiO$_2$ NWs, the Li$^+$ transference number of which is determined to be 0.62. Figure 4.8 (c) shows the comparison of the Li$^+$ transference number of CPEs with SP@TiO$_2$ NWs and TiO$_2$ NWs to pure PEO electrolyte. It can be clearly seen that the Li$^+$ transference number of the two types of CPEs is much higher than that of pure PEO electrolyte (0.41), and the CPE with SP@TiO$_2$ NWs is even higher than that of the CPE with TiO$_2$ NWs (0.56). These results suggest that the addition of nanofillers can increase the Li$^+$ transference number due to the surface interactions between the nanofillers and ions/polymers.$^{[162]}$ Namely, the polymer-nanofiller interaction can facilitate segment movement, leading to promoted Li$^+$ mobility and increased Li$^+$ transference number. More importantly, the core-shell SP@TiO$_2$ NWs can further improve the Li$^+$ transference number.
transference number, possibly due to the unique interactions between protein and ions. To investigate the role of protein in interacting with ions, we added excessive LiClO$_4$ salts into the dispersion of SP@TiO$_2$ NWs and rinsed the NWs several times by ethanol to remove residual LiClO$_4$. The EDS mapping was performed to probe the distribution of Cl element (Li element cannot be detected by EDS). As shown in Figure 4.8 (d), Cl element is clearly distributed on the SP@TiO$_2$ NWs, which suggests that the SP@TiO$_2$ NWs can adsorb considerable ClO$_4^-$.

In our previous studies$^{[164]}$, we demonstrated through molecular dynamic simulations that protein was able to strongly interact with ClO$_4^-$ or ClO$_4$ clusters by the positively charged amino acid residues to form protein-ion complex. Through the above studies, we can speculate that the strong interactions between protein and ions especially anions can greatly assist in immobilizing ClO$_4^-$, resulting in improved Li$^+$ transference number of the CPEs.

![Graphs and Diagrams](image-url)
Figure 4.9. The role of protein in dissociating lithium salts and promoting ion-conduction. (a) – (c) FTIR spectra of PEO electrolyte and CPEs with TiO$_2$ NWs and SP@TiO$_2$ NWs as well as the Gaussian–Lorentzian fitting curves of the ClO$_4^\text{-}$ absorbance; (f) Comparison of the ClO$_4^\text{-}$ states in different CPEs as compared with pure PEO electrolyte; (g) Schematic illustration of protein ion-conduction channel promoting dissociation of lithium salts and conduction of Li$^+$. Loading of nanofillers in all CPEs: 10 wt%.

The above results indicate that protein plays a critical role in interacting with ions and improving the electrochemical properties of the CPEs. To reveal how the SP@TiO$_2$ NWs bring about further improvement in ionic conductivity, we investigated the contribution of SP@TiO$_2$ NWs to dissociation of lithium salts. We recorded the FTIR spectra of various CPEs emphasizing the range of 590 ~ 655 cm$^{-1}$, which reflects the dissociation degree of the lithium salt, that is, LiClO$_4$. The FTIR spectra with Gaussian–Lorentzian fitting results of the CPEs with core-shell SP@TiO$_2$ NWs and TiO$_2$ NWs as well as pure PEO electrolyte are displayed in Figure 4.9 (a) – (c). As shown in the figure, for the three cases, two bands at about 623 and 635 cm$^{-1}$ can be clearly distinguished, which can be ascribed to free ClO$_4^\text{-}$ and bonded ion pairs (Li$^+\text{ClO}_4^\text{-}$), respectively.$^{[153,222]}$ Therefore, the dissociation degree of LiClO$_4$ can be determined by the peak area ratio of the two bands. Based on the fitting results in Figure 4.9 (d), one can find that addition of nanofillers results in growth of free ClO$_4^\text{-}$ band and reduction of bonded ClO$_4^\text{-}$ band, which suggests a higher dissociation degree of the lithium salts. This is contributed by the fact that the nanofillers introduce Lewis acid-base interactions between the nanofillers and the ions, which benefits the dissociation of lithium salts and increases the fraction of free Li$^+$. More specifically, the CPE with SP@TiO$_2$ NWs reveals the highest percentage of free ClO$_4^\text{-}$ (83.7%), as compared to the CPE with TiO$_2$ NWs (76.6%) and PEO electrolyte (71.7%). This indicates that SP@TiO$_2$
NWs remarkably improve the dissociation of Li$^+$ClO$_4^-$ ion pairs due to the unique interactions between protein and ions as revealed in above studies.

The possible mechanism on how the protein interacts with ions and thereby enhances the ionic conductivity is illustrated in Figure 4.9 (e). The abovementioned studies demonstrate that protein can adsorb a large number of ClO$_4^-$ anions due to electrostatic interaction by positively charged amino acid residues. This strong interaction can promote dissociation of lithium salts, which leads to improvement in Li$^+$ mobility and thereby ionic conductivity. Meanwhile, the “locked” ClO$_4^-$ clusters by protein significantly improve the Li$^+$ transference number and on the other, help to transport Li$^+$ owing to their attraction to Li$^+$. More specifically, a possible ion-transport model is proposed as revealed by our previous study$^{[164]}$, that the oxygen atoms in protein backbones and “locked” ClO$_4^-$ clusters along the protein chain serve as numerous coordination sites allowing and promoting the hopping of Li$^+$ among then due to the strong attraction force toward Li$^+$. As a result, the protein performs as a unique fast ion-conduction channel on the TiO$_2$ NW surface, which effectively improves the Li$^+$ transference number and ionic conductivity of the CPEs simultaneously.

4.3.4 Battery performance

To reveal the advantages of the improved mechanical properties by SP@TiO$_2$ NWs, two types of CPEs loaded with 10 wt% SP@TiO$_2$ NWs and SP-TiO$_2$ NPs were sandwiched between two lithium metals to perform lithium plating/stripping testing. Note that for fair comparison, the thickness of both CPEs is controlled to be ~ 70 µm. As shown in Figure 4.10 (a), the circuit in the cell assembled with CPE containing SP-TiO$_2$ NPs shorts at the 18$^{th}$ cycle, which is due to the poor mechanical properties of the CPE especially at high temperature. On the contrary, the SP@TiO$_2$
NW cell undergoes more than 70 cycles without circuit-shorting and shows much lower overpotential than that of the SP-TiO₂ NP cell. This result implies that the SP@TiO₂ NWs effectively reinforce the mechanical properties of the CPE and serve as strong “frameworks” that help to prevent the penetration of lithium dendrites through the CPE. Figure 4.10 (b) displays the specific voltage profiles of the 9 ~ 10th and 51 ~ 52nd cycles, the flat plateaus of which suggest a very smooth Li plating/stripping process[223], contributed by the decent ionic conductivity of the CPE at the elevated temperature.

Figure 4.10. (a) Voltage profiles of Li/CPE/Li cells at various current densities. (b) Voltage profiles of the 9 - 10th and 51 – 52nd cycles of the Li/CPE (SP@TiO₂ NWs)/Li cells.
Additionally, we further examined the electrochemical performance of the CPEs with SP@TiO$_2$ NWs in half cells and the cells were tested at 65 °C. As displayed in Figure 4.11 (a), the cells function normally and stably at various current rates and exhibit typical voltage profiles of LiCoO$_2$. Figure 4.11 (b) depicts the C-rate performance of the cells. As is shown, the capacity slightly decays from ca. 135 mAh/g to ca. 122 mAh/g when increasing the current rate from 0.2 C to 0.5 C, followed by a little higher capacity decay to ca. 111 mAh/g when the current rate further increases to 1 C. Subsequently, the capacity recovers to ca. 137 mAh/g once the current rate decreases to 0.2 C. This result indicates that the cells are able to deliver appropriate capacities at small or moderate current rates without notable capacity loss, due to the fact that the CPE acts as both an ion-conductor and a separator. The cycle stability of the cell tested at 0.3 C is shown in Figure 4.11 (c). It is found that the cell with the CPE loaded with SP@TiO$_2$ NWs delivers the highest capacity at all tested cycles as compared with the ones with SP-TiO$_2$ NPs and TiO$_2$ NWs, owing to the superior ionic conductivity of the SP@TiO$_2$ NWs loaded CPE that allows a smooth ion-transport between the two electrodes. More specifically, all the CPEs present a noticeable capacity decay in the first couple of cycles especially for the cases of SP-TiO$_2$ NPs and TiO$_2$ NWs. This is contributed by complicated factors such as unstable contact between the electrode and electrolyte or the formation of unknown solid electrolyte interphase between the Li metal and the new electrolyte. By contrast, the CPE with SP@TiO$_2$ NWs shows very stable capacity, which demonstrates to have a capacity retention of 94.7% after 70 cycles and an average Coulombic efficiency of 98.6%. The above studies indicate that the high ionic conductivity and good mechanical properties of the CPEs due to the core-shell SP@TiO$_2$ NWs contribute to the excellent electrochemical performance of the half cells running at high temperature.
Figure 4.11. (a) Voltage profiles of half cells with CPE loaded with 10 wt% SP@TiO$_2$ NWs at various current rates. (b) C-rate performance of half cells with CPE loaded with 10 wt% SP@TiO$_2$ NWs. (c) Cycle stability of half cells with CPEs loaded with 10 wt% SP@TiO$_2$ NWs, SP-TiO$_2$ NPs and TiO$_2$ NWs tested at 0.3 C. All the measurements were performed at 65 °C.

4.4. Conclusions

In summary, a type of core-shell SP@TiO$_2$ NWs is fabricated via protein-functionalization on electrospun TiO$_2$ NWs, i.e. in-situ growing protein shell on the TiO$_2$ NWs. With the novel SP@TiO$_2$ NWs, the ionic conductivity, mechanical properties, electrochemical stability and even Li$^+$ transference number of the CPEs are significantly enhanced. Compared with the counterpart,
SP-TiO$_2$ nanoparticles, it is found that the core-shell SP@TiO$_2$ NWs more effectively improve the ionic conductivity and mechanical properties of the CPEs, owing to the more continuous networked-structure of the one-dimensional NWs.
CHAPTER 5

PROTEIN-BASED BINDERS FOR HIGH-ENERGY LI-S BATTERIES

5.1 Introduction

Lithium-ion batteries with high energy-density and capacity have continuously dominated the energy storage market in multiple industry sectors such as electric vehicles, portable electronics, large-scale power supply systems. Among various rechargeable battery systems, lithium-sulfur (Li-S) batteries have received ever-increasing attention due to their superior advantages in specific capacity (1675 mAh/g)[224] and energy density (2600 Wh/kg)[225], which are five times higher than that of conventional lithium-ion batteries based on intercalation compound cathodes (e.g. LiFePO₄, LiCoO₂, LiMn₂O₄).[95,226] However, before the practical use of Li-S batteries, several critical challenges need to be overcome, which mainly originate from: (1) insulating nature of S and polysulfides, which limits the electronic transport inside the S cathode bulk; (2) dissolution and diffusion of polysulfides leading to shuttling effect, which consumes active materials and reduces capacity; (3) large volume change of S during cycling (~ 80%) that disrupts the integrity and structural stability of S cathode.[96,98,227] Aiming to address these issues, considerable efforts have been focused on constructing advanced composite S cathodes, which mainly involves encapsulating S into a carbon host such as hollow carbon spheres[228–230], porous carbon[231–233], graphene[234–236], carbon nanotubes[237–239], carbon nanofibers[240–243], or their heteroatom-doped derivatives[108,244–247]. These attempts have made substantial progress on solving some aspects of the problems and pushed forward the engineering of Li-S batteries. However, the critical shortcomings of these strategies are involving complicated and costly fabrication processes
and usually applicable to low loading level of the active materials, making them not appropriate for broad practical applications.

Despite of its low loading percentage (usually < 10 wt%) in an electrode, binder is a crucial component binding active materials and conductive fillers together to form conductive networks around active materials and glue them with the current collector. At the same time, binder is essential for controlling the overall microstructures (e.g. porous structure, interfaces and conduction networks), mechanical properties and structural integrity of an electrode.\textsuperscript{[125,248]} In particular, for high-capacity electrodes such as S cathode, binder plays a critical role in maintaining the structural integrity and stability of the S cathode, which can be significantly damaged by large volume change of S and dissolution of the intermediates (polysulfides) during lithiation/de-lithiation process.\textsuperscript{[87,249]} Thus, a mechanically strong binder is highly desired by advanced S cathodes. More importantly, the easy dissolution and diffusion of polysulfides in an organic liquid electrolyte calls for additional functions of the binder beyond mechanical robustness, such as adsorbing the polysulfides, in order to confine the active materials within the cathode region to alleviate the shuttling effect. Therefore, rationally designing a suitable binder is of great significance for enhancing the properties of S cathodes. A traditional binder such as poly(vinylidene fluoride) (PVDF) acts as a simple “physical adhesive” enabling mechanical connection between S active materials and conductive fillers, but it lacks the capability of binding polysulfides, despite of its excellent mechanical/electrochemical stability. In this regard, tremendous endeavors have been devoted to developing various advanced robust and functional binder materials.

Over the past few decades, polar polymers have been extensively studied as they can offer strong adsorption of polysulfides via dipolar interactions.\textsuperscript{[92,250,251]} For example, Liu et al.\textsuperscript{[252]}
demonstrated a cross-linked network binder of sodium alginate-Cu with strong chemical binding effects with polysulfides and good mechanical properties to significantly improve the electrochemical performance of the resulting S cathode. Another example was reported by Chen et al.\cite{95} who developed a hydrophilic functional binder of PPA, which was able to strongly anchor polysulfides and presented excellent mechanical properties resulting in a high-loading S cathode. In addition to polar polymers, recently ionic polymers have emerged as one type of promising binder materials that can provide electrostatic interactions with polysulfides.\cite{253} Namely, a type of polycation binder (PDAT) reported by Su et al.\cite{254} was demonstrated to possess very strong interactions with polysulfides due to its positively charged backbone and the polysulfide anions. Zeng et al.\cite{255} revealed a multi-dimensional polycation β-cyclodextrin (β-CDp-N\textsuperscript{+}) binder, in which the cations could help immobilize polysulfides, and the hyperbranched network structure could accommodate the volume change. In addition to abovementioned binder materials with improved mechanical properties and adsorption of polysulfides, some other unique binders endowed with additional functions have been of great interest. For example, PEDOT:PSS-Mg\textsuperscript{2+}\cite{91}, PEB\cite{256}, comb-like PSPEG\cite{257}, etc., which themselves possess electrical or ionic conductivity, have been reported to make great contributions to the electrochemical performances. In a nutshell, developing multi-functional binder materials with superior mechanical properties is in critical need by advanced high-performance S cathodes, which is extremely important for scalable production.

Based on these considerations, in this work we design and fabricate a new multi-functional binder based on soy protein (SP) incorporated with poly(acrylic acid) (PAA), which integrates high mechanical strength, strong polysulfide anchoring and good ion-conduction capability. The synergistic effects and intermolecular interactions between the two materials result in a robust and multi-functional network binder. With the use of this multi-functional binder, an advanced S
cathode with improved microstructures, robust and porous conduction networks facilitating good ion-conduction, and excellent confinement of polysulfides is achieved. As a result, the mechanical properties and electrochemical performances (e.g. specific capacity, cycle stability, C-rate performance) of the S cathode are significantly improved. Furthermore, we surprisingly find that good and stable performances can be realized on high-loading S cathodes (above 5 mg/cm\(^2\) loading of S), which deliver comparative areal capacities with commercialized lithium-ion batteries. The roles that the multi-functional binder play in the improvements of the properties/performances of the S cathodes are systematically analyzed and verified by density functional theory (DFT) calculations.

5.2 Experimental

5.2.1. Sample preparation

(1) Preparation of SP-PAA network binders: SP powders (donated by Archer Daniels Midland) were first denatured in an acetic acid solution with a pH value of 2 at 95 °C under stirring for 1 h. The denaturation process was able to significantly reduce the particle size of SP to nanoscale.\(^{[258]}\) The solid concentration of the solution was 3 wt%. Then the SP solution was cooled down to room temperature naturally for subsequent experiment. At the same time, a PAA solution with a concentration of 3 wt% was prepared by dissolving PAA powders (Mw = 450,000 g/mol, Sigma Aldrich) in the acetic acid solution (pH = 2) under stirring until completely dissolved. Afterward the above two solutions were mixed together according to a weight ratio of SP : PAA = 3 : 2 and stirred for 1 h at room temperature. In this mixing process, the formation of hydrogen bonding occurred to generate SP-PAA network binder. The prepared mixture solution of SP-PAA was used as the binder for subsequent experiments.
(2) Fabrication of S cathodes with various binders and cell assembly: Three types of binder solutions: SP, PAA, and SP-PAA, with a solid concentration of 3 wt% were used to fabricate S cathodes. Briefly, the S cathodes were prepared by mixing 67.5 wt% S particles (Sigma Aldrich), 22.5 wt% carbon black (SuperC45, MTI) and 10 wt% binder in a mortar and the mixture was milled for 15 min to form homogeneous slurry. The slurry was casted onto a carbon-coated aluminum foil by a doctor blade controlling the thickness and was dried at room temperature for 1 h. The obtained electrode laminates were punched into 0.5-inch circular disks with various S loadings and were further dried in a vacuum oven for 12 h to completely remove the residual solvents and moisture prior to being transferred to the argon-filled glove box. 2032-type coin cells were assembled with the Celgard (PP/PE/PP, trilayer) separator by using a liquid electrolyte solution composed of 1 M LiTFSI dissolved in mixed solvents of DOL/DME (1 : 1 by volume) with 2 wt% LiNO₃ as additive. The electrolyte/sulfur ratio was kept constant to be 10 µL/mg.

(3) Preparation of Li₂S₆ solution and visualized adsorption testing: To prepare Li₂S₆ solution (0.05 mM), a certain amount of Li₂S powders (Sigma Aldrich) and S powders were added into the mixed solvent of DOL/DME (1 : 1 by volume) according to a molar ratio of 1 : 5. The mixture was vigorously stirred at 50 °C for 3 h in the argon-filled glove box to finally obtain the Li₂S₆ solution. To demonstrate the adsorption ability of various binders, composites of binder/CB were first prepared with a mass ratio of 1 : 1. Various binder solutions and CB particles were mixed in a mortar uniformly and dried at room temperature. The composites were further dried in a vacuum oven for removing residual solvents and moisture and were transferred into the argon-filled glove box. For the visualized adsorption testing, 0.1 g composites were added into 10 mL Li₂S₆ solution in the glove box.
(4) Density functional theory (DFT) calculation: The molecular simulations were carried out at the B3LYP 6-31+G(d,p) level of DFT using Gaussian 5.0, based on the previous study[259]. The geometries of the molecules were first optimized to the minimum energy. For SP simulations, multiple amino acid sequences were randomly picked according to the PDB file (ID: 1UIK). For each amino acid sequence, at least three different types of amino acids were included to finally cover 18 kinds of amino acids of SP in total. The adsorption binding energy (Ea) was computed to inspect the binding energy of Li$_2$S with N and O atoms in the segments of PAA and various amino acids. It is assumed that only one N or O atom interact with Li ion of Li$_2$S. Ea can be determined via eqn. 5.1:

\[
E_a = E_{Li_2S} + E_{polymer} - E_{Li_2S+polymer}
\]  

(eqn. 5.1)

where $E_{Li_2S}$, $E_{polymer}$, and $E_{Li_2S+polymer}$ refer to the minimized ground-state energies of Li$_2$S, polymer and the complex of Li$_2$S and polymer, respectively.

5.2.2. Characterization

(1) Characterizations of binders: Infrared spectra of the solid binder films were recorded by a Fourier transform infrared spectrophotometer (FTIR) (Nicolet iS10) using ATR mode. The viscosity of the various binder solutions (5 wt%) was measured by a viscometer (Brookfield) and the tip rotation speed was kept constant to be 10 RPM. Dynamic mechanical analysis (DMA) was used to examine the storage modulus of the solid binder films in frequency-strain mode at 1 Hz. The liquid electrolyte uptake of the binder films was measured by immersing the films in a liquid electrolyte solution and weighing the mass of the films at varying time intervals. When taking the films out for weighing, the residual liquid electrolyte was carefully wiped away by Kimwipes tissue. The liquid electrolyte uptake was determined via eqn. 5.2:
\[ \eta = \frac{m_a - m_0}{m_0} \times 100 \]  

(eqn. 5.2)

Where \( \eta \) (%) refers to the liquid electrolyte uptake; \( m_0 \) and \( m_a \) refer to the mass of the film before and after immersing in the liquid electrolyte, respectively.

(2) Characterizations of electrodes: The morphology of the free surfaces of electrodes was investigated by scanning electron microscopy (SEM, Quanta 200F). The mechanical properties of the electrodes were tested by a rheometer (HR-2, TA Instruments) via indentation and stress-relaxation. In a typical measurement, the electrodes before and after immersing in a liquid electrolyte for 5 min were attached onto the sample holder. Meanwhile, a steel tip (diameter: 8 mm) kept approaching toward the electrodes with a constant speed of 1 \( \mu \)m/s until reaching a maximum axial force of 25 N. Then the tip stopped moving and stayed static for 2 min. The variation of axial force in the whole process was recorded with time. The adhesion property of the electrodes was investigated by a peel-off testing carried out using the same rheometer. The electrodes were first tightly attached on the sample stage by a double-sided tape. Then a 3M tape was adhered to the electrode surface, with an effective contact area of 1.5 cm\(^2\) (1 cm \( \times \) 1.5 cm), while the other side of the 3M tape was tightly fixed to the steel tip. The steel tip with the tape kept moving upward with a constant speed of 300 \( \mu \)m/s. The evolution of axial force was recorded until the electrode laminate completely detached from the current collector. The electrical conductivity of the electrodes under dynamic shearing was recorded by a SourceMeter (Keithley 2410). The setup is shown in Figure 5.6 (c). The dynamic shearing was generated by a rheometer that can precisely control the frequency and strain amplitude to produce various deformation intensities (see the inset table in Figure 5.6 (d)). The SourceMeter was connected with the rheometer, recording the evolution of electrical conductivity with various deformation rates. The electrical
conductivity was obtained via $\sigma = l/RA$, where $l$ is the thickness of the electrode; $R$ is the resistance determined by the SourceMeter; $A$ is the effective area of the electrode contacting with the tip (50.24 mm$^2$).

(3) Electrochemical characterization: The charging/discharging curves, cycle stability and C-rate performance of the Li-S cells were obtained via cycling the cells with a cut-off voltage of 1.5 – 2.8 V by using a battery analyzer (BST8-MA, MTI) at room temperature. Electrochemical impedance spectroscopy (EIS) was used to measure the impedance spectra of the Li-S cells by an electrochemical workstation (CHI 660E) in a frequency range of 0.01 - 1 M Hz. The open-circuit voltage of the Li-S cells was measured by using an electrochemical workstation via the Open Circuit Potential mode at various time intervals.

5.3 Results and discussion

5.3.1 Conceptual design

Binder is a critical ingredient for controlling the overall electrode structures in batteries. In particular, for S cathodes that experience a dramatic volume change and dissolution of S active materials, the binder becomes the only “soft” material that can buffer the deformation and help to stabilize the electrode structures. Traditional binders such as PVDF, in spite of their acceptable adhesion and good electrochemical stability, are insufficient for both accommodating the large volume change and preventing the diffusion of polysulfides, due to the nonfunctionalized chain structures. Consequently, the microstructures of the S cathode will be greatly destroyed and meanwhile, the shuttling effect will still occur. Therefore, building robust conduction networks with good ability of anchoring polysulfides around S active materials is believed to be an effective strategy to stabilizing S cathodes. This is realized by applying a multi-functional robust binder
demonstrated in this work. As depicted in Figure 5.1 (a), we design a new multi-functional robust binder by capitalizing the merits of two materials: soy protein (SP) and poly(acrylic acid) (PAA). As is well known that a number of polar groups (e.g. amine, carboxyl, carbonyl groups, etc.)\textsuperscript{[260]} has been proved to possess strong binding effect with polysulfides due to dipolar interactions. SP as a natural protein, possesses 18 different kinds of amino acids, making it rich in various polar functional groups. The abundant functional groups of SP enable it to strongly adsorb polysulfides with mitigating the irreversible dissolution of polysulfides. Also, SP presents a good ionic conductivity (ca. 10\textsuperscript{-5} S/cm, 25 °C) as revealed by our previous study\textsuperscript{[164]}, which can promote the transport of Li\textsuperscript{+} in the S cathode bulk to significantly boost the electrochemical reactions especially at high current densities. This is because the oxygen atoms in the protein backbone and the negatively charged amino acids (Arg. and Lys.) that attract anions (e.g. ClO\textsubscript{4}\textsuperscript{-}) perform as coordination sites, enabling fast hopping of Li\textsuperscript{+} among them. At the same time, PAA is a widely-used aqueous binder material that possesses certain ability of binding polysulfides\textsuperscript{[87,261]}. In addition to this property, we explore that PAA presents superior mechanical properties and is conducive to form stable interfaces between S active materials and conductive fillers, thus resulting in robust conduction networks around S particles. Due to the strong interactions between SP and PAA, a multi-functional network binder is fabricated with integration of strong polysulfide anchoring, robust mechanical properties and good conduction of Li\textsuperscript{+}, which tremendously enhances the mechanical properties and electrochemical performances of the S cathode as illustrated in Figure 5.1 (b). The synergy of the multi-functional binder will make great contribution to the transport of ions/electrons, structural stability of S cathode and adsorption of polysulfides.
Figure 5.1. Schematic illustration of the design strategy of the robust and multi-functional binder (SP-PAA) via incorporating two functional materials. (a) Illustration of the design concept for fabricating the multi-functional robust binder by taking advantage of two functional materials. (b) Schematic of the structural changes of S cathodes with a multi-functional robust binder during lithiation/de-lithiation process. Note: PS refers to polysulfide.

5.3.2 Binder properties

As shown in Figure 5.2 (a), the Fourier-transform infrared spectroscopy (FTIR) was performed to investigate the interactions between SP and PAA. It can be found that the FTIR spectrum of PAA reveals several characteristic peaks at 1167, 1413, 1452 and 1717 cm\(^{-1}\) attributed to C-O stretching, C-O-H in-plane bonding, -CH\(_2\) stretching and C=O stretching, respectively.\(^{262,263}\) SP shows multiple dominant peaks at 1246, 1536 and 1645 cm\(^{-1}\), which can be
assigned to C-N stretching (amide III), N-H bending (amide II) and C=O stretching (amide I), respectively.\textsuperscript{[264,265]} Regarding their combination, SP-PAA, it can be seen that the FTIR spectrum displays the characteristic peaks of SP and PAA, indicating the existence of both materials. In particular, one finds notable peak shift for SP-PAA. Specifically, the peaks originally at 1536, 1645 and 1717 cm\textsuperscript{-1} respectively corresponding to N-H bending (amide II), C=O stretching (amide I) and C=O stretching obviously move to 1539, 1648 and 1708 cm\textsuperscript{-1} after incorporation of SP and PAA. This indicates that there is a very strong intermolecular interaction between -NH group of SP and -COOH group of PAA via forming hydrogen bonding as shown in Figure 5.2 (b). The strong intermolecular interaction eventually results in the formation of network structure by SP and PAA, contributing greatly to the mechanical properties of the resulting SP-PAA binder. In addition, as shown in Figure 5.2 (c) the viscosity of the SP-PAA solution (545 mPa.s) is remarkably higher than the calculative viscosity (CV) (378 mPa.s) determined by the mass ratio of SP and PAA in SP-PAA (3 : 2), which also proves the intermolecular binding effect between SP and PAA.\textsuperscript{[85]}
Figure 5.2. (a) FTIR spectra of SP, PAA and SP-PAA. (b) Schematic of the formation of hydrogen bonding between PAA and SP. (c) Viscosity of SP, PAA and SP-PAA solutions (5 wt%) at 25 °C. Calculative viscosity (CV) is calculated based on the mass ratio of SP and PAA in SP-PAA (3 : 2). (d) Storage modulus of SP, PAA and SP-PAA solid films obtained by DMA tensile mode at 25 °C. (e) Liquid electrolyte uptake of SP, PAA and SP-PAA solid films at 25 °C.

The mechanical properties of the binder play an important role in buffering the volume deformation that the S cathode will experience over alloying/de-alloying process with Li. We measured the storage modulus of the various solid binder films by dynamic mechanical analysis (DMA) to be compared with PVDF film. As displayed in Figure 5.2 (d), of the four types of binder films, PAA presents the highest modulus of 1.78 GPa that is about twice that of SP (0.91 GPa). At the same time, SP-PAA reveals a modulus of 1.39 GPa, only slightly lowered by SP, which is also higher than that of PVDF with a modulus of 1.15 GPa. The high modulus of SP-PAA is significantly contributed by the robust network structure derived from the strong intermolecular interactions between SP and PAA. Further, for actual battery applications, the liquid electrolyte uptake of the binder is another critical factor considerably affecting the electrode structures and electrochemical performances of the batteries. An appropriate uptake level of liquid electrolyte will be beneficial for maintaining the structural stability and integrity of the electrodes and constructing fast ion-transport pathways inside the electrodes simultaneously. We inspected the liquid electrolyte uptake of the SP, PAA and SP-PAA solid films by immersing them in the electrolyte solution (1 M LiTFSI dissolved in DOL/DME (1 : 1 by volume)) and calculating the weight gain over specific time intervals. The results are displayed in Figure 5.2 (e). It is found that SP is not able to adsorb any liquid electrolyte over all timeframe, showing negligible liquid electrolyte uptake. On the contrary, PAA can remarkably uptake more liquid electrolyte (ca. 30%),
while SP-PAA presents a medium electrolyte uptake of ca. 9%. The aforementioned results indicate that two points are worthy of discussion here. Firstly, the trifling electrolyte uptake of SP helps to maintain the mechanical properties of SP and thereby the structural stability of the S cathodes in batteries; however, on the other hand, it impedes the permeation of liquid electrolyte and the construction of ion-conduction pathways around the S particles. Secondly, although PAA shows high electrolyte uptake level, which benefits the ion-conduction inside the S cathodes, the mechanical properties of the PAA binder itself and the resulting S cathodes will be sacrificed accordingly. Thus, the combination of SP and PAA may result in a proper electrolyte uptake level that assists in maintaining a good balance between mechanical properties and ion-conduction capability, which will be discussed in detail later.

5.3.3 Electrode properties
Figure 5.3. Microstructures of S cathodes with different binders. (a) – (c) SEM images of the S cathodes with SP, PAA and SP-PAA as the binder, respectively. (d) – (f) Illustration of the structures of the S cathodes prepared with SP, PAA and SP-PAA, respectively.

We surprisingly find that the SP-PAA binder effectively improves the electrode microstructures such as uniformity, porous structure and interfaces. In specific, for the S cathode with SP, the SEM images in Figure 5.3 (a) show many cracks on the electrode surface indicating a very poor structural integrity. In addition, one finds that the conduction networks around S particles are very weak with poor interfaces and even big cracks between S particles and conductive fillers (carbon black, CB). In contrast, PAA is found to effectively improve the
structural properties of the S cathode. As shown in Figure 5.3 (b), the microstructure of the S cathode dramatically changes as compared with the case of SP. It can be seen that the electrode presents a very uniform overall microstructure and no noticeable cracks can be observed. Taking a closer look, the CB particles are well distributed around S particles, forming much improved interface quality between them. Moreover, it is revealed that the composite of CB and PAA in the S cathode leads to a relatively compact porous structure with good uniformity and contact with S particles, generating stable conduction networks around S particles. In the case of SP-PAA shown in Figure 5.3 (c), one can observe that the accumulation of CB particles is much looser than that of PAA electrode yielding more big pores on the electrode surface with a generally uniform structure, which significantly helps the permeation of liquid electrolyte. Meanwhile, the CB particles encompass around the S particles generating stable interfaces and highly-porous and robust conduction networks.

The structural properties of the S cathodes as discussed above, including uniformity, porous structure and interfaces, tremendously impact the charge-transport, structural stability of the electrodes and absorption of polysulfides in charging/discharging process. For the S cathode prepared with SP as illustrated in Figure 5.3 (d), even though SP shows strong polysulfide adsorption capability that will be discussed in detail later, its poor structural integrity with numerous cracks and weak interfaces between S particles and CB results in very unstable structures of the S cathode when experiencing notable volume change during cycling. As a result, the overall integrity of the electrode and the conduction networks for ions/electrons are ruined; meanwhile, the polysulfides still diffuse out of the S cathode eventually. In contrast, PAA and SP-PAA can remarkably improve the structural factors, and thus the mechanical/electrochemical properties of the S cathodes. As demonstrated above, PAA helps form uniform electrode structures
and robust conduction networks around S particles. Such improved microstructures benefit the mechanical and structural stability of the S cathode. In addition, the robust conduction networks built from PAA/CB assist in binding the dissolved polysulfides due to some interaction between PAA and polysulfides as reported previously[261] (see Figure 5.3 (e)). Nonetheless, the less porous structure of the electrode may impede the permeation of liquid electrolyte to the electrode bulk. As further improvement, SP-PAA does not only give rise to uniform electrode structures (e.g. stable interface, good porous structure, etc.) contributing to mechanical properties and charge-transfer of the electrode, but also strong capability of binding polysulfides in Figure 5.3 (f). Such strong binding capability is enabled by the various functional groups of SP (to be demonstrated in detail later) and advanced porous conduction networks that maximize the function of SP-PAA for adsorbing polysulfides.

Figure 5.4. Mechanical properties of dry S cathodes. (a) – (b) The evolution of compression stress versus indentation time for as-prepared S cathodes with different binders, measured by compression and stress-relaxation.
It is well established that the mechanical properties of electrodes, especially high-capacity electrodes such as S cathode, are extremely important for device applications. Therefore, good mechanical properties and structural stability are imperative for advanced S cathodes that are a result of comprehensive contributions from the electrode microstructure factors (e.g. uniformity, porous structure, interfaces, etc.). We have demonstrated that the microstructures of the S cathodes are significantly impacted by the various types of binders, and PAA and SP-PAA result in much uniform electrode structures. To elaborate the advantages of the specific binders, we further investigated the mechanical properties of the S cathodes before and after immersing in liquid electrolyte via rheological measurement. The measurement includes two stages: compression and stress-relaxation. In the first stage, compression stage, a metal tip with a diameter of 8 µm continuously approaches he electrode at a constant moving speed of 1 µm/s. In this process, the compression stress steeply grows with the compression strain until reaching an axial force of 25 N. Afterward, the tip stops moving and keeps a constant compression strain, and in this stress-relaxation stage, the compression stress gradually decays with time. The stress-relaxation stage can reveal how stable the electrode is after undergoing indentation and a certain compression strain, which is a reflection of mechanical and structural stability of the electrode. More detailed information about the testing can be found in Experimental section.

**Figure 5.4 (a) and (b)** shows the evolution of compression stress with time in stress-relaxation process for the dry S cathodes with different binders. The decay behavior of the compression stress can be well-fitted via eqn. 5.3:

\[
\sigma = m (1 + t)^n
\]  

(eqn. 5.3)

where \(\sigma\) is the compression stress and \(t\) is the time. Constants \(m\) and \(n\) are relevant to the decay rate of the compression stress. It is believed that the faster the decay rate, the poorer the structural
stability. It can be seen in Figure 5.4 that the S cathode with PAA shows the slowest decay rate of compression stress, with the smallest absolute values of m and n: 0.62, 0.04, respectively. However, SP is found to exhibit the fastest decay rate revealed by the largest absolute values of m (0.64) and n (0.06). SP-PAA presents a medium decay rate (absolute values of m and n are 0.63 and 0.05, respectively). The results are in good agreement with the morphological studies and the moduli of the binders as discussed above. For example, PAA possesses the highest modulus (1.78 GPa) and PAA electrode shows very uniform microstructures and stable interfaces, all of which are responsible for the best mechanical properties of dry PAA electrode.

![Figure 5.5](image)

**Figure 5.5.** Mechanical properties of wet S cathodes. (a) – (b) The evolution of compression stress versus indentation time for wet S cathodes with different binders, measured by compression and stress-relaxation. Prior to testing, the electrodes were soaked in liquid electrolyte solution for 5 min.

Moreover, the mechanical properties of the S cathodes after immersing in the liquid electrolyte for 5 min were also examined, in order to simulate the actual conditions in batteries. As shown in Figure 5.5 (a) and (b), wetting of the liquid electrolyte deteriorates the mechanical properties of all electrodes, which is verified by the substantially increasing absolute values of
both $m$ and $n$. However, it is surprisingly found that SP-PAA electrode outperforms the PAA electrode in wet-state and delivers the best mechanical properties, which presents the smallest absolute values of $m$ and $n$ (1.21 and 0.22, respectively). In addition, the PAA electrode even shows much poorer mechanical properties than that of the SP electrode with much larger absolute values of $m$ and $n$ as compared with the SP electrode. The dramatically reduced mechanical properties of the PAA electrode after immersing in the liquid electrolyte mainly result from the notable swelling of PAA in the liquid electrolyte as revealed in Figure 5.2(e). In a word, SP-PAA makes great contributions to the mechanical properties of the electrode from two aspects. Firstly, the use of SP-PAA results in robust electrode microstructures with good uniformity, porous structures and good interaction on interfaces. These structural features effectively reinforce the mechanical and structural stability of the S cathode. Secondly, SP-PAA presents an appropriate swelling property in liquid electrolyte, which assists in maintaining the overall structural characteristics and mechanical properties of the S cathode after wetting by the liquid electrolyte.
Figure 5.6. (a) Peel force versus displacement for the S cathodes with different binders by peel-off testing. (b) Comparison of peel off force for S cathodes with different binders. (c) Illustration of the setup for measuring the electrical conductivity of S cathodes affected by dynamic shearing. (d) The effects of dynamic shearing on the electrical conductivity of the S cathodes with different binders at varying D-rates (the inset table shows the specific parameters for adjusting the D-rate).

In addition to mechanical properties, strong adhesion of the electrode laminate to the current collector is critically required for realizing stable and high-performance batteries. In this work, the adhesion property of the electrodes was studied by peel-off testing using a 3M tape. The peel forces against displacement for various S cathodes are shown in Figure 5.6 (a) and the obtained peel forces are summarized in Figure 5.6 (b) in comparison with the S cathode with the
PVDF binder. It clearly reveals that the peel force of SP electrode is the highest (ca. 1.5 N), and PVDF electrode renders the lowest peel force of only ca. 0.6 N. The peel force of the SP-PAA electrode is found to be a little lower than that of the SP electrode, which is ca. 1.3 N. The abovementioned results indicate that SP provides very strong adhesion to the current collector, which should be attributed to its abundant functional groups including polar/nonpolar and charged groups. The various kinds of functional groups bring about rich interactions with the current collector, i.e. Van der Waals force, charge-charge interaction, etc., to effectively reinforce the adhesion between the electrode and the current collector.\cite{[118,211]} Thus, the existence of SP in SP-PAA can significantly improve the adhesion property of the SP-PAA electrode.

For high-capacity electrodes such as S cathode, construction of robust and stable conduction networks is crucial during electrochemical reactions, as the large volume change will severely impact the conduction pathways. As revealed above in morphological studies, three types of binders lead to distinctly different microstructures, i.e. uniformity/interfaces. To interpret the significance of the electrode structures in the stability of conduction networks, we measured the electrical conductivity of the electrodes while applying dynamic shearing force on the electrodes. As illustrated in Figure 5.6 (c), the setup includes a rheometer generating dynamic shearing on the electrode and a SourceMeter recording the electrical conductivity of the electrode. Here, a series of deformation rates (D-rates) is applied via varying the parameters including frequency and strain according to eqn. 5.4:

$$D\text{-rate} = f \times \varepsilon \times 100$$  \hspace{1cm} (eqn. 5.4)

where \( f \) refers to frequency and \( \varepsilon \) refers to strain. The detailed D-rates studied here are listed in the insert table in Figure 5.6 (d). The variation of electrical conductivity versus D-rate is also shown
in Figure 5.6 (d). Basically, the electrical conductivity of all electrodes declines with increasing intensity of deformation due to growing breaking-down of conduction structures. In specific, the PAA and SP-PAA electrodes deliver very similar electrical conductivities with moderate deformation, e.g. ≤ 1D. When the deformation enlarges to 1D and 5D, the PAA electrode outmatches the SP-PAA electrode, due to the much better mechanical properties of the dry PAA electrode as revealed above in mechanical properties studies. In addition, owing to the poor mechanical properties and conduction network structure of the SP electrode, the electrical conductivity evidently lies in the lowest level of the three electrodes. In short, the PAA and SP-PAA electrodes present much better and more robust conduction network structures as compared with the SP electrode, which greatly stabilizes the conduction structures of the electrodes under deformation and potentially promotes the electrochemical performances of the electrodes.

To prove the effectiveness of the SP-PAA binder in improving the electrode structures, mechanical properties and thereof electrochemical performances of the S cathodes, Li-S cells with different S cathodes were assembled and tested. The S cathodes with a moderate loading of active material about 1.5 mg/cm² were first evaluated. The charging/discharging curves of various S cathodes measured at 0.1 A/g are displayed in Figure 5.7 (a). As shown, as compared with the PVDF electrode, SP, PAA and SP-PAA electrodes present remarkably higher discharge capacities. This is because PVDF fails to capture dissolved polysulfides, leading to great loss of S active materials. In specific, the SP-PAA electrode delivers the highest capacity of 1308 mAh/g, while the lowest capacity of 969 mAh/g is brought about by the PVDF electrode. Moreover, one finds that the SP-PAA electrode shows the lowest polarization with a flat discharge plateau at 2.1 V, indicating that the electrochemical reactions occur very smoothly owing to the good electrode microstructures with advanced conduction networks. Importantly, the intrinsic ionic conductivity
of SP, as revealed by our previous study\cite{164}, promoting the transport of Li$^+$, also helps to facilitate the electrochemical reactions. At the same time, the PAA electrode reveals the highest polarization and the SP electrode shows a medium one. This is because the compact accumulation of CB particles with less porous structure and notable swelling of PAA in liquid electrolytes, greatly increases the resistance for charge-transport and deteriorates the structures of the PAA electrode. Figure 5.7 (b) shows the voltage profiles of the SP-PAA electrode upon various cycles at 0.5 A/g. The eight voltage profiles show very good repeatability, despite of slight capacity decay with increasing cycles, which suggests that the electrochemical reactions turn out very stable and reversible during cycling.

The improvement of electrode structures significantly contributes to the electrochemical performances especially the C-rate performance. As displayed in Figure 5.7 (c), the capacities of the S cathode with SP-PAA are distinctly the highest of all S cathodes at all tested current densities. In specific, the capacities of SP-PAA electrode recover to ca. 1105 mAh/g when the current density decreases from 1 A/g to 0.2 A/g, which is 99.4% of the original capacities of ca. 1112 mAh/g at 0.2 A/g. The recovery ratios for SP and PAA electrodes are 98.8% and 98.9%, respectively, which are much lower than that of SP-PAA electrode. Moreover, the role of the electrode structures becomes more dominant at high current densities, as the porous conduction-network structures are essential for realizing fast charge-transport. It is specially found that at a high current density of such as 1 A/g, SP-PAA electrode still exhibits the highest capacity of ca. 686 mAh/g as compared with the electrodes with SP (ca. 578 mAh/g) and PAA (ca. 371 mAh/g). The result implies that the advantages of the enhanced structures and mechanical properties of SP-PAA electrode significantly improve the C-rate performance and enable a smooth and fast charge-transport even at high current densities.
Figure 5.7. Electrochemical performance of the batteries with different S cathodes. (a) Voltage profiles of S cathodes with different binders at 0.1 A/g. (b) Voltage profiles of the S cathode with SP-PAA as the binder upon varying cycles at 0.5 A/g. (c) C-rate performance of S cathodes with different binders. (d) Nyquist plot of S cathodes with different binders. (e) Cycle stability and Coulombic efficiency of S cathodes with different binders at 0.5 A/g.
The benefits of SP-PAA to the electrochemical performances were further inspected by electrochemical impedance spectroscopy (EIS). The Nyquist plot of different S cathodes is shown in Figure 5.7 (d). The result indicates that the SP-PAA electrode exhibits the lowest charge-transfer resistance of about 52 Ω, which can be defined as the diameter of the semi-circle in the high-frequency area arising from the interface between electrode and electrolyte.\textsuperscript{[266,267]} The PAA electrode presents the highest charge-transfer resistance of ca. 172 Ω, while SP electrode reveals a much lower one (ca. 83 Ω). The lowest charge-transfer resistance of the SP-PAA electrode can be ascribed to two reasons: (1) the uniform electrode microstructure with robust porous conduction networks; (2) the good ion-conduction of SP that further facilitates the transport of Li\textsuperscript{+}. As a result, the charge-transport inside the SP-PAA electrode can be effectively promoted, which is consistent with the above electrochemical performances.

Figure 5.7 (e) shows the cycle performance of the electrodes at 0.5 A/g. It is noticeably found that the SP-PAA electrode delivers the highest capacity among all electrodes. Meanwhile, the capacity of the SP-PAA electrode is very stable upon 200 cycles without evident capacity fading, presenting a high average Coulombic efficiency of 99.3%. It is also found that SP and PAA electrodes exhibit very similar capacity within about 120 cycles, although the capacity of the SP electrode apparently decays in the first couple of cycles due to the instability of the electrode by electrochemical reactions possibly. Also, an obvious capacity decay occurs on PAA electrode after about 130 cycles caused by the severe shuttling effect during cycling. The average Coulombic efficiencies of SP and PAA electrodes are determined to be 98.2 and 97.1%, respectively, which are much lower than that of the SP-PAA electrode. The above results suggest that the binder and the electrode structure play a critical role in diminishing the loss of S active materials and shuttling effect. For the SP-PAA electrode, owing to its uniform microstructure and good interfaces between
S particles and CB particles, as well as the strong adsorption of polysulfides by SP-PAA, the Coulombic efficiency is substantially improved, which finally results in very stable cycling with minimized shuttling effect.

![Figure 5.8](image)

**Figure 5.8.** (a) Open-circuit voltage (OCV) of S cathodes with different binders. (b) Photographs showing various composites of binder/CB in Li$_2$S$_6$ solution.

To further demonstrate the ability of SP-PAA to anchor polysulfides and preventing the diffusion of them, the self-discharge behavior of the S cathodes was monitored. It is well known that Li-S batteries usually suffer from severe self-discharge mainly resulting from the diffusion of polysulfides.[268,269] The open-circuit voltage (OCV) of various freshly made S cathodes was recorded with time, the decay of which can reflect the self-discharge behavior of the electrodes.[270] As shown in **Figure 5.8** (a), the OCVs of the fresh cells with SP, PAA and SP-PAA are found to be 3.04, 2.85 and 2.99 V, respectively. After resting for 3 days, the OCVs of all cells drop down due to some diffusion of polysulfides. Specifically, the SP and SP-PAA cells present declined OCVs of 2.87 and 2.88 V, respectively. The OCV of PAA cell, however, very obviously decreases to only 2.36 V. The OCVs become steadier subsequently and after 21 days of rest, SP-PAA cell
shows the highest OCV retention of 96%, while the retentions of SP and PAA cells are 91 and 83%, respectively, much lower than that of the SP-PAA cell. The result indicates that SP and SP-PAA being the binder function as effective absorbents of polysulfides to significantly reduce the self-discharge. The strong binding effect with polysulfides by SP-PAA and uniform interfaces/conduction networks among S particles and SP-PAA/CB composite should be the main reasons accounting for the smallest self-discharge of SP-PAA cell.

The digital photo in Figure 5.8 (b) also proves the advantage of SP and SP-PAA for adsorbing polysulfides. As displayed, various composites of binder/CB with same mass were immersed in Li$_2$S$_6$ solution with DOL/DME (1 : 1 by volume) as the solvent to demonstrate the effect of different binders for adsorbing polysulfides. It is found that the addition of three types of binder/CB composites effectively absorb polysulfides, which can be confirmed by the color change of the Li$_2$S$_6$ solution from yellow to lighter yellow or even transparent. Importantly, the polysulfide adsorption ability of SP/CB and SP-PAA/CB is much better than that of PAA/CB, due to the fact that the color of Li$_2$S$_6$ solution becomes completely transparent for them, while the solution is still yellowish for PAA/CB case.

The above results suggest that as compared with PAA, both SP and SP-PAA have stronger capability of binding polysulfides. In order to verify the polysulfide binding effect of PAA and SP, the adsorption binding energy ($E_a$) of them is calculated by using density functional theory (DFT). The schematic structures of the representative polysulfide, Li$_2$S, adsorbed by PAA and specific amino acids are depicted in Figure 5.9 (a) – (c), in which one active atom (O, N) is assumed to interact with one Li ion of Li$_2$S. In regard to PAA (Figure 5.9 (a)), the adsorption of Li$_2$S is realized by carbonyl group and the binding energy is determined to be 1.115 eV. As SP possesses enormous structures and complicated amino acid sequences, to simplify the calculation of the
binding energies of SP, multiple amino acid sequences with at least three different types of amino acids included in each sequence are randomly chosen, and finally 18 kinds of amino acids in total are calculated. It is also noted that as amino acid obtains both amine and carboxyl groups, O and N atoms are both taken into consideration. Take Histidine and Serine for example, **Figure 5.9 (b) and (c)** shows the optimized geometries for adsorption of Li$_2$S by the amino acids via O or N atom. One finds that the binding energies of Histidine and Serine with Li$_2$S are 1.381 and 1.457 eV respectively, both of which are much higher than that of PAA. **Figure 5.9 (f)** summarizes the adsorption binding energies of all amino acids of SP with Li$_2$S via O and N atoms in comparison with PAA. It is surprisingly found that a majority of amino acids such as His., Ser., Gly., Lys., Glu., Arg., etc. show much higher binding energies with Li$_2$S. In particular, those aforementioned amino acids actually dominate the composition of SP. For instance, the contents of Glu., Asp., Arg., Lys. in SP are 19.1, 11.6, 7.6 and 6.3 wt%, respectively. The DFT calculation results confirm that SP offers much stronger interactions with polysulfides as compared with PAA, which is consistent with experimental demonstration.
Figure 5.9. (a) Optimized geometries and adsorption binding energy (Ea) of Li$_2$S adsorbed by PAA. (b) Optimized geometries and Ea of Li$_2$S adsorbed by Histidine via oxygen atom. (c) Optimized geometries and Ea of Li$_2$S adsorbed by Serine via nitrogen atom. (d) Summary on the adsorption binding energies of various amino acids of SP with Li$_2$S via either oxygen or nitrogen atom as compared with PAA.

Aiming to achieve high-energy Li-S batteries, high loading level of S active materials is a prerequisite. In this work, therefore, we examine the high-loading S cathodes with various binders. As shown in Figure 5.10 (a), with a higher loading of S such as ca. 2.8 mg/cm$^2$, all cells work normally at a small current density of 0.05 A/g. However, when enlarging the current density to 0.1 A/g shown in Figure 5.10 (b), only SP-PAA cell functions well exhibiting typical charging/discharging curves of Li-S batteries. Both SP and PAA cells fail to ensure smooth and
stable electrochemical reactions, as can be reflected by the unstable voltage profiles with large polarization. It is worth noting that SP-PAA electrode is able to deliver stable performance even at a further increased S loading.

**Figure 5.10.** Voltage profiles of S cathodes with 2.8 mg/cm$^2$ S loading. (a) – (b) Charging/discharging curves of S cathodes with different binders at 0.05 and 0.1 A/g, respectively.

As shown in **Figure 5.11 (a)**, with an S loading of 5.6 mg/cm$^2$, the SP-PAA electrode demonstrates stable voltage profiles at various current densities. At the same time, the polarization doesn’t visibly enlarge with the increasing current densities, except for the case of 1 A/g. The superior performance is contributed by the good mechanical properties, robust and porous conduction networks and effective polysulfide-confinement of SP-PAA electrode, as well as good ion-conduction of SP-PAA, which significantly assist in maintaining structural stability of the electrode and promoting the electrochemical reactions.
**Figure 5.11.** Electrochemical performance of Li-S batteries with high S loading. (a) Voltage profiles of S cathode with SP-PAA with a high loading of S: 5.6 mg/cm². (b) C-rate performance of S cathodes with SP-PAA with various loading of S. (c) Cycle stability of S cathodes with SP-PAA with various loading of S.

**Figure 5.11 (b)** displays the C-rate performance of S cathodes with SP-PAA with various S loadings: 2.8, 5.6 and 9.4 mg/cm². It can be seen that the higher the loading of S, the poorer the rate performance. In other words, the S cathode with an S loading of 2.8 mg/cm² delivers the highest capacities over all tested current densities. In the case of 5.6 mg/cm² S loading, the
capacities are stable over various current densities, and 97.3% capacity can be recovered when switching back the current density from 0.5 to 0.2 A/g. Furthermore, the cycle stabilities of the three electrodes at 0.3 A/g are compared in Figure 5.11 (c). Both electrodes with 2.8 and 5.6 mg/cm² active materials present very stable capacity during cycling and no obvious capacity fading can be observed. Particularly, in the case of 5.6 mg/cm² loading of S, a high capacity of 826 mAh/g (areal capacity of 4.6 mAh/cm²) is delivered and maintained as 725 mAh/g after 100 cycles. Additionally, the electrode with extremely high loading of S (9.4 mg/cm²) exhibits a satisfactory capacity of 701 mAh/g in the beginning and retains around 610 mAh/g during cycling, corresponding to an areal capacity of 5.7 mAh/cm² that is much higher than commercialized lithium-ion batteries (ca. 4 mAh/cm²)[27,250]. One still finds, however, relatively unstable capacities for such S cathode, due to the structural instability by severe volume deformation which is a critically challenging task for high-loading S cathodes.

5.4 Conclusions

This study has demonstrated a cost-effective strategy for fabricating a multi-functional binder by facile incorporation of two functional materials: soy protein and poly(acrylic acid). This advanced binder shows high mechanical strength, strong polysulfide adsorption and good ion-conduction ability. The results indicate that soy protein is effective for adsorbing polysulfides due to its rich functional groups, and meanwhile its robustness helps to buffer the volume change of S. Additionally, its ion-conduction ability promotes the electrochemical reactions. With the use of this binder, high loading S cathodes are achieved, and excellent battery performance is delivered.
CHAPTER 6

PROTEIN NANOFILTER FOR TRAPPING POLYSULFIDES AND
PROMOTING LI⁺-TRANSPORT IN LI-S BATTERIES

6.1 Introduction

The rapid development of portable electronics, electric vehicles and stationary storage systems\(^{[96,271,272]}\) raises an urgent demand for advanced energy storage devices. Over the past years, substantial efforts have been made to develop various advanced battery systems such as lithium-ion (Li-ion) batteries, sodium-ion (Na-ion) batteries, lithium-air and lithium-sulfur (Li-S) batteries.\(^{[110,273-275]}\) Among these systems, Li-S batteries have received considerable attention due to their remarkable advantages including high theoretical energy density (2600 Wh/kg),\(^{[261]}\) high specific capacity (1675 mAh/g),\(^{[99]}\) low cost and environmental benignity. However, major challenges exist limiting their applications. The practical energy density, rate capability and especially cycling stability of Li-S batteries have been severely limited by several factors, including poor electron-/ion-conductivity of S-related species, diffusion of intermediate polysulfides and large volume changes.\(^{[28,29,276]}\) In particular, the shuttle effect, which results from the dissolution and migration of the polysulfides (Li\(_2\)S\(_n\), 4 ≤ n ≤ 8) during charge/discharge process, is believed to be one of the main reasons for rapid capacity fading and low columbic efficiency.\(^{[277-279]}\) Dissolution of polysulfides gradually consumes the sulfur active material and creates more “dead” S-species. Also, the polysulfides on the Li-metal surface can be reduced to Li\(_2\)S, which will deposit on the Li-metal surface and affect the uniformity and dynamics of lithium ion
deposition on the Li-anode. Therefore, most of the efforts have been focused on how to suppress the diffusion of polysulfides and various strategies to reduce diffusion have been reported.

One strategy is to introduce blocking function inside the sulfur cathode. To do so, nanomaterials with blocking function for the diffusion of polysulfides are usually employed to form special composites with sulfur. Various core-shell structures have been reported to confine sulfur active materials. Different conductive materials and methods have been employed to construct such structures, for example, graphene-wrapped sulfur cathode, porous carbon/sulfur composites, hollow-structured sulfur materials and sulfur nanoparticles with conducting polymer as the shell, etc. Although these conductive shells can greatly improve the initial capacity and utilization of sulfur, they still experience a fast capacity decay in initial cycles, indicating that they are insufficient to prevent the dissolution and diffusion of polysulfides. In addition, fabrication of the core-shell structures is usually difficult to scale up or be cost-effective, which hinders their practical applications. In order to enhance the blocking function, new nanomaterials showing stronger interactions with polysulfides have been reported, which include nitrogen-doped carbon-based nanomaterials (such as graphene, carbon nanotubes, etc.), WS$_2$ nanosheets and metal oxides (e.g. Ti$_4$O$_7$), etc.

In addition to above approaches, introducing an additional layer traditionally called interlayer, to block the diffusion of polysulfides is also one feasible strategy. Two main methods have been reported to produce this interlayer. The first method is to create a separator coating. Various materials, including carbon-based conductive nanomaterials (such as carbon black, carbon nanotubes and graphene), polymers (such as Nafion) and metal oxide nanoparticles have been employed to coat the surface on either the separator side or the S-cathode side. Among these coating materials, the separator coated with a conductive nanomaterial
shows better improvement than the non-conductive coating such as an Al₂O₃ nanoparticle coating. Similarly, the second method is to insert an individual interlayer, usually a freestanding thin layer of conductive materials (such as carbon fiber cloth and carbon paper), between the S-cathode and the separator. In this method, the interlayer is designed and fabricated independently.

In summary, creating advanced nanostructures to block the diffusion of polysulfides remains the most promising strategy to address the shuttle effects without sacrificing the intrinsic advantages of the batteries. In particular, the introduction of a conductive interlayer is one of the most cost-effective methods. Meanwhile, the interlayer in a form of either a surface coating or an individual free-standing film can be easily integrated into the current fabrication technology for lithium ion batteries. Therefore, the design of an advanced multi-functional interlayered structure is critical for developing high-performance metal-sulfur batteries. An ideal interlayer for enhancing metal-sulfur battery performance should have several properties: strong interactions with polysulfides for trapping them, low resistance for lithium-ion transport, high electron-conductivity allowing electrochemical reactions of trapped polysulfides, good mechanical and electrochemical stability as well as compatibility with other components in the Li-S system.

6.2 Experimental

6.2.1 Sample preparation

(1) Preparation of polymer-nanoparticle dispersion and separator wet-coating: i. Protein/CB dispersion. The gelatin protein (from porcine skin, Type A, Sigma Aldrich, Mw = 50,000 ~ 100,000 g/mol) was first dissolved in DI water or mixture of acetic acid (AA) and DI with weight ratio of AA/DI of 8:2 and pH of 2. The gelatin concentration was fixed as 3 wt%.
Conductive nanoparticles, e.g. carbon black (MTI corp.), were then mixed with the gelatin solution with a loading of 50 wt% in the final protein/CB nanocomposite with the aid of ultrasonication to obtain homogeneous dispersion. In this case, gelatin works as a type of surfactant to disperse the nanoparticles. To improve the homogeneity, stability and flexibility of the resultant coating, a small amount of poly(ethylene oxide) (2 wt%) (Mw = 5,000,000 g/mol, Sigma) was added into the gelatin/CB dispersion, and then uniformly mixed by vigorous stirring for about 30 min. The suspension was casted onto the commercial separator (Celgard, PP/PE/PP, trilayer) by a film applicator (Dr. Blade) and then dried at room temperature to remove the solvents. 

**ii. PVDF/CB dispersion.** PVDF (Mw = 560,000 g/mol, Sigma Aldrich) was dissolved in N-Methyl-2-pyrrolidone (NMP) solvent with a concentration of 5 wt%. Then CB was mixed with PVDF solution by bowl mill for ca. 10 min. Two different CB loadings were used, e.g. 50 wt% and 80 wt%, designated as PVDF-CB50% and PVDF-CB80% respectively, to adjust the porous structures of the coating. The coating layers were dried at 60 °C for ca. 12 hours to remove the solvent. The final thickness of all the nanocomposites coating was controlled to be in the range from 6 to 7 µm. The loadings of carbon black in the separator coatings are: 0.23±0.01 mg/cm² for gelatin-CB, 0.13±0.02 mg/cm² for PVDF-CB80% and 0.11±0.02 mg/cm² for PVDF-CB50%.

(2) S cathode preparation and Li-S cell assembly: The S-cathode was prepared by mixing 67.5 wt% sulfur powders (Sigma), 22.5 wt% carbon black and 10 wt% PVDF in NMP as solvent. The slurry was then casted onto aluminum foil and dried at 50 °C overnight. The loading of active material was controlled around 1.6 mg/cm². Another control S-cathode was prepared by mixing 47 wt% sulfur powders, 47 wt% carbon black and 6 wt% PVDF following the same procedures. For Li-S cell assembly, all the materials including bare separator and nanocomposites coated separators (PSNF@CS, PVDF-50%CB@CS and PVDF-80%CB@CS) and S-cathode were further...
dried in vacuum oven at 60 °C for 12 hours to remove residual solvent and moisture, and then transferred into argon-filled glove box. The liquid electrolyte solution was composed of 1 M LiTFSI dissolved in mixed solvents of DOL and DME (1:1 by volume) with 2 wt% LiNO₃ as additive. One droplet of liquid electrolyte was applied onto the S-cathode and anode (lithium metal) surfaces respectively to ensure wetting. The electrolyte/sulfur ratio was kept constant around 3.8 mL/g. In the case of nanocomposites coated separators, the coated side was placed facing the S-cathode in order to trap the dissolved polysulfides. All these components were compressed under pressure of 500 psi in a coin cell (CR2032, MTI Corp.).

6.2.2 Characterization

(1) Morphology, wetting property and porosity characterizations: The morphology of all the samples was characterized by Scanning Electron Microscopy (SEM) (Quanta 200F). The wetting property of the suspension on the commercial separator was characterized by contact angle by using OCA 15 plus contact angle analyzer. The suspensions were prepared with the same solid concentration to generate droplets. The commercial Celgard separator (PP/PE/PP, trilayer) was used as substrate and five measurements at different locations were done to ensure consistency. The porosity of the nanocomposites was measured via n-butanol uptake. The nanocomposites were prepared by coating the various CB dispersions on aluminum foils by Dr. Blade. The thickness of all the dried nanocomposite coatings was controlled around 8 µm. The weight of the nanocomposites was measured before and after immersion in n-butanol for 2 h. The porosity of the nanocomposites was calculated via eqn. 6.1:

\[
\text{Porosity} = \frac{(m_b/\rho_b)}{(m_b/\rho_b + m_p/\rho_p)} \times 100\% \quad \text{(eqn. 6.1)}
\]
where \( m_b, m_p \) are the weight of n-butanol and nanocomposites, and \( \rho_b, \rho_p \) are the density of n-butanol and nanocomposites, respectively.

(2) Mechanical properties measurement: The gelatin/CB and PVDF/CB dispersions (loading of CB: 50 wt\%) were casted on Al foil by Dr. Blade. The thickness of the dry nanocomposites was controlled around 10 \( \mu m \). The mechanical properties were measured by using a rheometer (HR-2, TA Instruments) via indentation. Briefly, the nanocomposite samples were placed on a sample holder. A steel tip with a diameter of 8 mm on the top was moving toward the sample at a constant speed of 1 \( \mu m/s \) until reaching a maximum axial force of 35 N. The axial force was recorded with time.

(3) Electrochemical testing: The electrochemical performance of the Li-S cells was examined by cycling the cells between 2.8 and 1.5 V by using a battery analyzer (BST8-MA, MTI) at room temperature. Electrochemical impedance spectroscopy (EIS) was used to measure the impedance of the cells via an electrochemical workstation (CHI660E) over a frequency range of 0.01-10\(^6\) Hz.

(4) Pressure drop testing: The pressure drop of the separator samples was measured by a manometer (UEi, EM201-B) under different flow rates controlled by the home-made set-up as illustrated in Figure 6.12 (a). The air flow rate was controlled by a syringe and a pump employed for electrospinning. A circular separator sample with a diameter of ca. 37 mm was placed in a homemade sample holder to perform pressure-drop testing.

6.2.3. Simulation studies

(1) Molecular structure of \( \text{Li}_2\text{S}_4 \): To simplify the simulation, only \( \text{Li}_2\text{S}_4 \) which is an intermediate product of the discharge process in Lithium-Sulfur batteries was studied in this work.
An accurate coordinate file of Li₂S₄ is required for a molecular simulation. Due to the insufficient data from experiments, all structure information is obtained from the first principle calculation. In order to fully understand the discharge mechanism in Lithium-Sulfur batteries, plenty of quantum-chemical studies and first principle simulations have been studied and stable molecular structures of polysulfides have been discussed. In this study, a stable molecular structure of Li₂S₄ was taken from density functional theory (DFT) calculations in Jand’s work, which provides detailed bond lengths for Li-Li and Li-S, and those calculated bond lengths are in good agreement with the results obtained by Wang et al. The dihedral angle of S-S-S-S in Li₂S₄ was chosen from a similar structure of Na₂S₄ in Daly’s work. With all the information listed above, a molecular structure of Li₂S₄ can be described as Figure 6.1.

![Figure 6.1. Molecular structure of Li₂S₄ at stable state.](image)

(2) Force parameters of Li₂S₄: We performed MD simulations using the following general form of interaction potential between the different components.

\[
U = \sum_{\text{bonds}} K_b (b - b_0)^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} K_\phi (1 + \cos(n\phi + \phi_0))
+ \sum_{\text{nonbonded}} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{\epsilon \sigma_{ij}} \right\}
\]

(eqn. 6.2)
Where, $K_b$, $K_\theta$, $K_\phi$ are force constants; $b_0$, $\theta_0$ are equilibrium bond lengths and angles, $\phi$, $n$ are dihedral phases and periodicities. Intermolecular parameters $e_{ij}$, $\theta_{ij}$, $q_i$, $q_j$ are the Lennard-Jones well depth and radius between atoms $i$ and $j$, the partial atomic charge of atom $i$ and $j$, respectively. Force constant $K_b$ was estimated based on a simulated Raman Spectra data from Partovi-Azar’s work.\textsuperscript{306} $K_\theta$ and $K_\phi$ were chosen from similar angles and dihedrals to make sure those force constants can maintain the correct molecular structure of Li$_2$S$_4$ throughout the entire MD simulation. Partial charges on each atom considered in our simulation were determined from Jand’s simulation results.\textsuperscript{303} The van der Waal parameters of Li and S in Li$_2$S$_4$ were copied of Li from amber force field and S in S$_8$ from CHARMM force field, respectively.

(3) Computational setup: The interaction between polysulfide and protein filter in organic electrolyte was performed by Molecular dynamic simulation using GROMACS package (5.0.5 version)\textsuperscript{169} with CHARMM36 force field\textsuperscript{307} for 200 ns. Gelatin, a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones and animals was randomly placed at the bottom of a simulation box of ~77 x 77 x 77 Å$^3$, and the backbone was constrained throughout the simulation to mimic a fixed protein coating on the carbon black as a filter according to the experiment. The electrolyte [1,3-dioxolane (DOL) and Dimethoxyethane (DME)] were mixed with the ratio of 1:1 (V/V) as solvent, and 30 Li$_2$S$_4$ molecules were added to the bulk system. The CGENFF (CHARMM generalized force field) was used for DOL and DME electrolyte.\textsuperscript{308} The long-range Coulomb interactions were treated with the PME method, while the van der Waals (vdW) interactions were handled with a 1.2 nm cutoff distance. Periodic boundary conditions were applied in all three directions. The simulation system was prepared and visualized using PACKMOL\textsuperscript{171} and VMD\textsuperscript{172}, respectively.
6.3 Results and discussion

6.3.1 Design strategy

As is well known, air filters are designed to remove pollutants in air with low flow resistance. Inspired by the concepts in air filtration, we propose a protein-based nanofilter for filtering polysulfides in Li-S batteries with low Li⁺ transport resistance, namely polysulfide nanofilter (PSNF), as shown in Figure 6.2 (a). From a filter point of view, the main function of air filter is to trap the pollutants (e.g. particulate matter (PM) of various sizes, chemical vapors, etc.) and only allow clean air to pass through. An ideal air filter should achieve high efficiency for filtering pollutants but low air-flow resistance, or low pressure drop. Correspondingly, the polysulfides generated in Li-S batteries can also be treated as “pollutants”, and the PSNF in our work is designed to capture the polysulfides “pollutants” and meanwhile provide low resistance for Li⁺ transport. Such PSNF is realized by compositing proteins with conductive particles, followed by a protein-directed self-assembly process. Due to the unique self-assembled porous structures and surface properties, the PSNF efficiently works to selectively trap the polysulfides “pollutants”, and meanwhile promotes the Li⁺ transport between the two electrodes. As a result, significant improvements in electrochemical performance of Li-S batteries are achieved.

The dissolved polysulfides “pollutants” in Li-S batteries not only result in serious shuttle effects, but also deteriorate the electrolyte performance, such as the decreased ionic conductivity. Therefore, developing a high-performance PSNF is an attractive solution for resolving the polysulfides dissolution issues. It is noted that conductive and porous interlayers have been of great interest in Li-S systems as reported in previous studies, such as the ones showing strong affinity with polysulfides (e.g. MoS₂ nanomaterial coating). In spite of this fact, treating
polysulfides as “pollutants” and using the concepts from air filtration are novel and significant. This sets new requirements for the development of Li-S battery interlayers. As shown in Figure 6.2 (b) for an effective interlayer, the porous structures should be designed, and the surfaces should be functionalized, such that it cannot only trap and hold polysulfides, but also reduce separator/electrode resistance and facilitate fast Li$^+$ transport. Moreover, some approaches in air filtration may also be adopted in design, fabrication and even characterization of the new interlayers, as will be discussed in detail in this study.

**Figure 6.2.** Design and fabrication of polysulfides nano-filter (PSNF) based on self-assembled protein@CB nanocomposite. (a) Illustration of PSNF interlayer for filtration of polysulfides in Li-S cells. (b) Critical properties for achieving a high-performance PSNF. (c) Schematic of the facile bio-nanotechnology proposed in this study for the fabrication of PSNF with 3D porous structures and functional surface via protein-directed self-assembly.
The fabrication strategy for the proposed PSNF is illustrated in Figure 6.2 (c). As shown, the 3D porous structures of PSNF are generated via a protein-directed self-assembly process, which has been reported to be an attractive method to fabricate self-assembled nanomaterials. Here one of the abundant natural proteins, gelatin, has been adopted for assisting the assembly process. The specific gelatin-particle and gelatin-gelatin interactions will lead to a unique porous structure, and the trapping of polysulfides is realized through the interactions from the functional groups along the protein chain.

![Figure 6.3](image)

**Figure 6.3.** Wetting behavior of PVDF/CB dispersion on separator and microstructure of PVDF/CB coating. (a) Digital photo of casted PVDF/CB dispersion on separator. The inset is contact angle of PVDF/CB dispersion on separator. (b) – (c) SEM images of PVDF/CB nanocomposite.

### 6.3.2 Fabrication studies

We first investigate our PSNF by comparison with the traditional conductive coating, which have been widely employed to block the diffusion of polysulfides.[99,294] From processing standpoint, a good affinity of the coating material with the separator in both wet and dry states is a prerequisite to achieve a high-quality coating on the separator surface. Via coating the carbon
black (CB) dispersions onto separator surface, we investigated the wetting behavior of the dispersion and microstructure of the nanocomposite coating after drying. As shown in Figure 6.3 (a), for the control sample, polyvinylidene fluoride/CB (PVDF/CB), there are weak interactions between CB and PVDF, despite that the dispersion shows good affinity to the separator and good wetting properties with a small contact angle of 49°. However, as revealed by SEM images in Figure 6.3 (b) and (c), the PVDF/CB nanocomposite coating shows inhomogeneous microstructure with cracks, and inferior porous structure with a porosity of 33.7% (see Table 6.1).

Table 6.1 Physical properties of various CB-based nanocomposite coating

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>33.7</td>
<td>12.0</td>
<td>45.7</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>6.8</td>
<td>6.2</td>
<td>6.4</td>
</tr>
</tbody>
</table>

In contrast to PVDF/CB system, the proposed PSNF via gelatin/CB nanocomposite shows excellent wetting properties and better porous structures. As shown in Figure 6.4 (a), protein shows much stronger interactions with CB particles due to its functional groups\(^{[126]}\). However, interestingly the self-assembled porous microstructures highly depend on specific solvent environment. When we use deionized (DI) water as solvent (usually used for protein-based dispersion), the gelatin/CB dispersion shows a higher contact angle to the separator (60°) and wrapping behavior of the separator due to shrinkage during drying (see Figure 6.4 (b) and (c)).

More importantly, as shown in Figure 6.4 (d), the resulting gelatin/CB nanocomposite shows poor porous structures and most of the CB nanoparticles are severely covered by gelatin to finally result in a very low porosity of 12.0% as indicated in Table 6.1. It is noted that the wrapping behavior is significant in this study. Firstly, it indicates that the gelatin protein can bring about strong
adhesion with the substrate, which is critical for the stability of separator coating. Secondly, as shown in Figure 6.4 (a), there are numerous free protein chains in the gelatin/CB dispersion, which leads to strong hydrogen bonding and less gelatin chains attached onto the CB surface (Figure 6.4 (e)).

**Figure 6.4.** (a) Schematic illustration of situation for gelatin/CB by deionized (DI) water. (b) Digital photo showing gelatin/CB dispersion on separator. The inset is contact angle of gelatin/CB dispersion on separator. (c) Digital photo showing wrapping behavior of Celgard separator with gelatin/CB coating. (d) SEM images of gelatin/CB by DI. (e) Digital photo showing gelatin dissolved in DI water started to gel in 2 h.

However, this situation dramatically changed when we use aqueous acetic acid solution (pH = 2) to prepare the dispersion (Figure 6.5 (a)). As shown in Figure 6.5 (b), the wetting behavior of the dispersion is notably improved with smaller contact angle (51°) as compared with
the one in DI water (60°). In addition, the dried coating layer shows no wrapping behavior as indicated in Figure 6.5 (c), and a self-assembled porous nanostructure (Figure 6.5 (d)) with homogeneous gelatin coating on CB surface that shows the highest porosity of 45.7% (see Table 6.1) can be achieved. These results indicate that acetic acid can assist the protein coating onto the CB particles and prevent gelation of gelatin as illustrated by Figure 6.5 (e). This is important to realize the designed functional surface for the protein@CB nanocomposites as illustrated in Figure 6.2 (c). Based on the above fabrication studies, we find that dispersion of gelatin/CB in acetic acid solution represents a feasible method for fabrication of separator coating with good wettability, structure uniformity and 3D porous structures.

Figure 6.5. (a) Schematic illustration of situation for gelatin/CB (PSNF) by mixture solvent of acetic acid (AA) and DI water (AA/DI). (b) Digital photo showing gelatin/CB dispersion on separator. The inset is contact angle of gelatin/CB dispersion on separator. (c) Digital photo
showing Celgard separator with gelatin/CB coating. (d) SEM images of gelatin/CB by AA/DI. (e) Digital photo showing gelatin dissolved in AA/DI without gelation in 2 h.

6.3.3 PSNF properties

Good mechanical properties of the coating materials are demanded to ensure the stable performance for the batteries. In this work, we measured the mechanical properties of the PSNF and PVDF-CB composites via indentation method. The results are shown in Figure 6.6. In this measurement, a tip with flat surface kept compressing the coating materials at a constant speed of 1 µm/s until reaching a maximum compression force of 35 N. The evolution of compression force with time was recorded. As shown, in compression stage, the compression stress sharply increased due to the increasing strain. The growth rate, which was defined as the slope for compression, can reflect the compression modulus. It can be seen that the PVDF-CB50% composite shows only a slightly higher slope of 0.046 than that of the PSNF (0.041). This indicates that the PSNF shows comparable mechanical properties with PVDF-CB50%.
Figure 6.6. Compression stress versus indentation time for PSNF as compared with PVDF-CB50%.

Furthermore, to demonstrate its polysulfides filtration capability, we performed polysulfides diffusion test for the separators with and without PSNF coating and the results are shown in Figure 6.7. In the test, a bottle filled with dark yellow polysulfides-polluted liquid electrolyte (concentration of polysulfides: ca. 0.6 mol/L) and another bottle filled with clean liquid electrolyte were connected by the separator sample. The bare Celgard separator causes quick diffusion of polysulfides and the color of the originally clean liquid electrolyte changes notably after 2 h, as shown in Figure 6.7 (a). After 4 to 6 hours, the color becomes darker due to the increasing polysulfides concentration. In contrast as shown in Figure 6.7 (b), when the separator is coated with PSNF, the clean electrolyte is mostly clear up to 4 hours and then starts to become yellowish because of the oversaturation of polysulfides beyond the capacity of PSNF.
Figure 6.7. Polysulfides filtration studies by diffusion testing and molecular simulation studies. 

(a) Digital photos showing the diffusion process of polysulfides in a system separated by bare Celgard separator. (b) Digital photos showing the diffusion process of polysulfides in a system separated by PSNF coated Celgard separator. (c) – (d), Snapshots of the initial and final states (after 200 ns) of interactions between Li₂S₄ and gelatin in the liquid electrolyte, respectively. (e) – (f) Interactions between Li₂S₄ molecules and the oxygen atom from the backbone of gelatin, and the COO⁻ end groups.
To further understand the specific interactions between polysulfides and the gelatin coating at molecular level, we performed molecular dynamic simulations to study the adsorption process of polysulfides (e.g. Li₂S₄) onto the gelatin. Figure 6.7 (c) and (d) are the snapshots of the initial and final states during the adsorption process of Li₂S₄ onto gelatin. As shown the polysulfide molecules have been mostly adsorbed onto the protein surface in 200 ns. We also noted that the unique spatial structures of protein chains may form some special “molecular cages” for effectively trapping and accommodating the polysulfides, which is quite different from conventional chemical trapping. A closer look at the adsorption sites on protein surface in Figure 6.7 (e) and (f) shows that polysulfides can be attracted by the oxygen atoms in the backbone (Figure 6.7 (e)) and COO⁻ end groups in the protein chains (Figure 6.7 (f)) due to strong electrostatic interactions. Moreover, the side groups on the primary amino acids (e.g. proline, hydroxyproline) are short enough to make the oxygen atoms and COO⁻ end groups accessible to the polysulfides, which provide a great number of “active-sites” having strong affinity with polysulfides.

Figure 6.8. Unit structure of gelatin. The functional groups interactive with polysulfides are indicated in the red boxes.
It is noted that the PSNF after 4-hour exposure to polysulfides also showed some diffusion of polysulfides as shown in Figure 6.7 (b). This phenomenon is related to the filtration capacity of the filter. After about 4-hour absorption, the PSNF may reach its trapping capacity limit. The filtration capacity is a critical factor for the design of separator coating in Li-S batteries. It should match the loading of active materials in the sulfur cathode to prolong the life span of the Li-S cells. Based on the simulation results, the filtration capacity can be roughly estimated from the structure unit of gelatin\textsuperscript{[312]} (Figure 6.8) and molecular weight of gelatin (50,000 ~ 100,000 g/mol). Assuming that one functional group can only interact with one lithium polysulfide molecule, and all the gelatin chains in the separator coating (gelatin loading of 0.23 ± 0.01 mg/cm\textsuperscript{2} as employed in our work) are involved in the filtration, it is estimated that the PSNF can provide a filtration capability of ca. 18.3 mol/g. However, it should be noted that the actual capacity is affected by many other factors (e.g. surface area, temperature, current density, etc.), which will be investigated in future studies.
**Figure 6.9.** Charge/discharge profiles of Li-S batteries with PSNF-coated Celgard separator (PSNF@CS) as compared with control systems. (a) Initial charge/discharge profiles at a low current density of 0.1 A/g. (b) Charge/discharge profiles at a medium current density of 0.5 A/g. (c) Charge/discharge profiles of the Li-S battery with PSNF-coating at different current densities; (d) Comparison of the charge/discharge voltage drop at a current density of 0.1 A/g.

The effects of PSNF on battery performance by PSNF were further demonstrated in Li-S batteries. We first compared the initial charge/discharge capacity in **Figure 6.9 (a)**. It is well known that the initial discharge capacity is a key parameter reflecting the utilization percentage of
the sulfur active material. As shown, the Li-S battery with the PSNF-coated separator (PSNF@CS) gives rise to the highest initial discharge capacity of 1318 mAh/g at a current density of 0.1 A/g. This is almost 80% utilization rate of active materials since the theoretical capacity of sulfur is 1672 mAh/g. In contrast, the cell with the bare Celgard separator (CS) shows a much lower capacity around 770 mAh/g. These results indicate that the PSNF coating significantly improves the utilization percentage of the active material and effectively traps the dissolved polysulfides.

In addition, we also evaluated the specific capacity and compared with the case with traditional coating of PVDF/CB composites. Two different ratios between PVDF and CB have been considered. The first control sample is PVDF-CB50%@CS with 50 wt% loading of CB; the second control sample is PVDF-CB80%@CS with 80 wt% loading of CB. Higher loading ratio of CB will generate more porous structure and thus assist the Li$^+$ transport. As shown in Figure 6.9 (a) for the Li-S cell with PVDF-CB50%@CS, the initial discharge capacity is about 1279 mAh/g, which is close to that for the PSNF@CS. While, for PVDF-CB80%@CS, the initial discharge capacity is only about 934 mAh/g, which is much lower than that of PVDF-CB50%@CS. This result implies that the main mechanism for the PVDF-CB coating to suppress the diffusion of polysulfides is physical blocking. The PVDF-CB coating with a higher loading of PVDF (PVDF-CB50%@CS) can block more polysulfides and results in higher capacity, since a higher loading of PVDF in the PVDF/CB nanocomposites can generate less porous structures. This physical blocking mechanism usually will lead to a trade-off between blocking efficiency and ion-transport capability, which will be discussed later.

In addition to the higher initial capacity, the PSNF coating also significantly reduces the cell resistance and improve the capacity at different current densities. Figure 6.9 (b) shows the charge/discharge profiles of the Li-S cells under a medium current density of 0.5 A/g. As shown
the capacity decreases and the voltage drop between the charge and discharge plateaus increases remarkably when the current density increases from 0.1 A/g to 0.5 A/g. The Li-S cell with PSNF@CS shows the highest capacity of ca. 950 mAh/g and all the cells with conductive separator coating yield higher capacity than the cell with bare separator. Moreover, the capacity of the Li-S cell with PVDF-CB80%@CS overtakes that of the cell with PVDF-CB50%@CS. Meanwhile, the voltage profiles become more sensitive to the separator coating at higher current density. At 0.5 A/g, the second discharge plateau for the PSNF-coated cell is around 2.0 V, which is higher than that of the cell with bare separator. In contrast, the discharge plateaus drop down to around 1.7 V for the cell with PVDF-CB50%@CS, and 1.9 V for the cells with PVDF-CB80%@CS. These results indicate that a higher loading of PVDF results in a higher resistance for the ion transport due to the blocking effect from PVDF.

Figure 6.9 (c) shows the charge/discharge profiles for only the Li-S cell with the PSNF@CS at different current densities. The profiles are similar for all the current densities from 0.1 to 0.8 A/g. The voltage drop between the charge/discharge profiles increases notably only at a high current density, such as 0.8 A/g. In addition, the voltage drop between charge and discharge plateaus as defined in Figure 6.9 (d) is the lowest for the PSNF@CS cell (~ 0.17 V), compared with that of the cells with bare separator (~ 0.22 V) and PVDF-CB80%@CS (~ 0.30 V). The results suggest that the PSNF coating shows lowest cell resistance as compared with traditional separator.

The coating of PSNF also significantly impacts other electrochemical performances, including rate capability and cycle stability. There are basically two factors controlling rate capability, the transport efficiency of ions/electrons and the kinetics of the electrochemical reactions between the active materials and lithium ions. Here, the rate capability is primarily
controlled by the first factor since we have employed exactly the same sulfur cathode and liquid electrolyte. Therefore, the rate capability shown in Figure 6.10 (a) can well reflect the effects of different separator coatings on the ion and polysulfides transport. The PSNF@CS shows the best rate capability when compared with the two control samples. More specifically, the PSNF@CS results in much less capacity decay from 1100 mAh/g @0.2 A/g to 900 mAh/g @ 0.8 A/g. In addition, the rate capacity is quite stable at different current densities. In contrast for the cell with PVDF-CB80%@CS, the rate capacity at a current density of 0.5 A/g is unstable and keeps decaying. When increasing the current density to 0.8 A/g, the rate capacity dramatically drops to around 240 mAh/g, which is even lower than that of the cell with bare separator. This indicates that the conventional conductive coating PVDF/CB can improve the capacity, but not the rate performance. However, the PSNF coating can simultaneously improve the capacity and rate capability, due to the unique surface property and microstructures of PSNF. In specific, the presence of gelatin on CB surface provides strong capture capability for polysulfides, which effectively increases the utilization of active materials to improve the capacity. Meanwhile, the good porous structure of PNSF offers more pathways for transporting Li⁺, which significantly prompts the Li⁺-transport process at varying current rates.
Figure 6.10. Rate capability, cycle stability and impedance studies of the PSNF-coating as compared with other separator coatings. (a) rate capability comparison at varying current densities. (b) Cycle stability of Li-S cell with 47 wt% sulfur cathodes at 0.3 A/g. (c) Nyquist plots of fresh Li-S cells containing different separator coatings in a frequency range of 0.01-1M Hz.

To further confirm the polysulfides trapping function of PSNF in Li-S cell, we prepared another control S-cathode with 47 wt% sulfur loading. Considering the carbon black in the PSNF layer, C/S ratio is 1:1 at cathode. The result shown in Figure 6.10 (b) indicates that the capacity of 47 wt% sulfur cathode cell at 0.3 A/g is improved to be around 720 mAh/g simply by increasing the C/S ratio, but it is still far lower than 980 mAh/g for the cell with PSNF. These results confirm that the significant improvements of performance for the Li-S cell with PSNF are mainly
contributed by the gelatin coating. In addition to effectively trapping the dissolved polysulfides, the PSNF coating can also reduce the Li⁺ transport resistance. Figure 6.10 (c) shows the electrochemical impedance of the fresh cells. The Nyquist plots confirm that the PSNF coating can notably reduce the charge transfer resistance while the PVDF/CB coating increases it when compared with the bare separator and PSNF coated separator.

Figure 6.11. (a) cycle performance comparison at a current density of 0.3 A/g. (b) – (c) SEM images of PSNF before and after 200 cycles of charging/discharging, respectively.

Moreover, the cycle stability is also improved with PSNF. Compared with the PVDF-CB80%@CS cell, the PSNF@CS cell shows not only much higher capacity, but also better stability as shown in Figure 6.11 (a). After 200 cycles, 75% of the initial capacity is retained for
the PSNF@CS cell, while it is only 63% for the PVDF-CB80%@CS cell. Moreover, the SEM images in Figure 6.11 (b) and (c) further prove that the polysulfides are effectively trapped by PSNF interlayer as all the pores are filled with solid active materials. Meanwhile, the capacity becomes more stable at ca. 670 mAh/g after about 250 cycles for the PSNF@CS cell. The capacity retention after ~200 cycles is important for understanding the diffusion of polysulfides inside the cells. The decaying of the discharge capacities with cycling indicates that both the PSNF and PVDF coating are not able to completely suppress or block the diffusion of polysulfides into the liquid electrolyte. However, the decaying rate is much faster for PVDF-CB80%@CS cell, suggesting that the PSNF coating is more effective in trapping and holding the polysulfides than PVDF coating. For the bare separator, the discharge capacity is low and quite stable with cycling. This is due to the fact that, without coating a large amount of polysulfides dissolve into the liquid electrolyte during the first couple of cycles and the system quickly reaches the final equilibrium or saturation state.
Figure 6.12. Air and ions flow resistance studies of separator coatings. (a) Schematic of the home-made set-up for air-flow resistance testing of the separators w/ or w/o coating layer. (b) Pressure drop of the separators versus different flow rates. (c) Voltage drop versus different current densities for the Li-S cells with the separators. (d) – (e) Schematics showing the effects of separator coating on the ion-transportation for bare Celgard separator, separator with PVDF/CB nanocomposite coating, and separator with PSNF coating, respectively.

In air filtration, pressure drop tests are usually performed to characterize and evaluate the porous structures in air filters. Due to the similarities between pressure-driven flow in air filters and voltage-driven ionic transport across the porous separators, we carried out pressure drop tests for the separators with different coating materials to evaluate the effects of the interlayer porous structures on the Li\textsuperscript{+} transport. Figure 6.12 (a) shows our testing system, small and steady flows were produced in our tests to prevent the separators from breaking or damaging. The pressure
drops for three battery separators were tested with flow rates from 15 to 30 mL/min and the results are summarized in Figure 6.12 (b). As shown, the bare separator (CS) shows the lowest pressure drop among all separator samples throughout the tested flow rates, indicating that separator coating will inevitably increase the flow resistance. Comparing the two separators with nanocomposite coatings, PSNF coating yields much lower pressure drop at all the tested flow rates compared with PVDF/CB coating. Meanwhile, the pressure drop of PVDF/CB coated separator is more sensitive to the flow rates. Adding an extra layer of porous material will inevitably increase the flow resistance, but the resistance is much lower for PSNF coating compared with PVDF/CB coating. The results are consistent with the observations from SEM images, in which more pathways with larger pore sizes were observed in PSNF coating favoring the flow transport. Furthermore, we also performed the voltage drop tests for Li-S cells with different separators. As shown in Figure 6.12 (c), for the Li-S cells with PVDF/CB coated separators the voltage drop at different current densities is highest. This is consistent with the pressure drop testing, the extra coating layer will also reduce the ionic transport. Surprisingly, if we look at the Li-S cells with PSNF coated separator, the voltage drops are even smaller than that for cells with the bare separator. However, the pressure drops for separators with PSNF coating are much higher than that for bare separators (Figure 6.12 (b)).

The seemly “inconsistent” results between pressure drop and voltage drop tests suggest that new mechanisms exist affecting the ionic transport. Clearly as shown in Figure 6.12 (d) – (f), the voltage drop tests were performed using Li-S cells, where the separators with or without coating are in direct contact with the two electrodes by compression force during cell assembly. While the pressure drop tests was performed in an open condition. As shown in Figure 6.12 (d), with bare separator and under the compression force, the soft sulfur particles and CB agglomerates
can be squeezed and thus block the separator pores increasing the Li\(^+\) transport resistance. In case when PVDF/CB nanocomposite coating is employed, as shown in Figure 6.12 (e), the poor porous structures in PVDF/CB coating block more the pathways for Li\(^+\) transport leading to much higher resistance. This is consistent with the impedance results in Figure 6.10 (a). On the other hand, when the separator is coated with PSNF as shown in Figure 6.12 (f), the PSNF coating is in direct contact with S-cathode. The large number of pores with bigger pore sizes in in PSNF open up more pathways promoting Li\(^+\) transport. Therefore, adding a PSNF coating on the separator not only effectively traps the dissolved polysulfides, but also improves the separator-cathode contact and facilitates Li\(^+\) transport.

6.4 Conclusions

In summary, this study has reported a novel polysulfide nanofilter (PSNF) that is fabricated and functionalized by a natural protein (e.g. gelatin) to address the polysulfide diffusion issues in Li-S batteries. Interestingly, the protein-directed self-assembly leads to a unique porous structure of PSNF, which not only provides more pathways for ion-transport, but also accommodates more polysulfides. Importantly, the PSNF surfaces are functionalized by gelatin proteins, and our simulations and experiments show that PSNF can effectively suppress the shuttle effects from migration of polysulfides. As a result, the PSNF remarkably improves Li-S battery performances. Moreover, a simple and facile pressure drop test which is usually used for air filters, can be employed to evaluate the coating quality and predict its contribution to electrochemical performances.
CHAPTER 7

SUMMARY OF CONCLUSIONS AND OUTLOOK

7.1 Summary of conclusions

Designing safe and high-energy Li-based batteries is the significant goal for next-generation ESDs. This dissertation has demonstrated the applications of proteins for realizing this goal from two research aspects: (1) fabricating safe and solid-state electrolytes with high ionic conductivity and mechanical properties; (2) fabricating high-performance Li-S batteries with a focus of addressing the shuttle effect and improving electrode structures/properties. Taking advantage of multi-functionalities and unique configuration of proteins, we are able to design and fabricate various protein-based complexes and composites. They present superior physicochemical, mechanical and electrochemical properties. Additionally, proteins are found to show unique interactions with ions and electrochemical intermediates (e.g. polysulfides), making them (1) capable of transporting ions for high-performance solid electrolytes, and (2) excellent filtering/binder materials for addressing the critical issues of Li-S batteries. The studies have opened up a new route to exploiting proteins for fabrication of advanced battery components. The specific conclusions of each part of this dissertation are summarized below.

7.1.1 Protein-based solid electrolytes

The fabrication of protein-based solid electrolytes has demonstrated the unique interactions between protein and ions. Significantly, proper approaches for controlling the protein-ion complex structures can lead to superior protein-based solid electrolytes with high ionic conductivity and
good mechanical properties. According to experimental and simulation results, a list of conclusions are drawn as below.

(1) By controlling the loading of lithium salt and evaporation temperature, the morphologies and ionic conductivity of protein-ion complexes can be adjusted and optimized.

(2) The structures of protein-ion complexes can be greatly tuned by the evaporation temperature for removing the solvents. It is specifically found that, increasing the evaporation temperature (e.g. 40 °C) results in more flexible protein chains with stronger interactions with ions.

(3) In a more flexible protein-ion complex, the positively charged amino acids show strong interactions with anions (ClO$_4^-$) to form anion clusters. The conduction of Li$^+$ is dependent on and facilitated by the anion clusters and the oxygen atoms of peptide bonds.

(4) A decoupled ion-transport mechanism is proposed for explaining all the findings. The protein-ion complex (protein-based solid electrolyte) shows high ionic conductivity and mechanical properties simultaneously. An extremely high Li$^+$ transference number (ca. 0.93) is naturally achieved.

7.1.2 Protein/TiO$_2$ hybrid nanofillers for composite electrolytes

The studies on protein/TiO$_2$ nanofillers for fabricating composite electrolytes are based on the understanding of protein-ion complexes that present strong interactions with ions. Capitalizing on the unique interactions between protein and ions, protein/TiO$_2$ nanofillers in the forms of nanoparticles and nanowires are fabricated to enhance conventional polymer electrolytes. The introduction of such hybrid nanofillers improves the critical properties of the electrolytes, including ionic conductivity, mechanical properties, electrochemical stability, Li$^+$ transference
number and even adhesion properties. The specific conclusions drawn from the studies are listed below.

(1) An effective and simple approach is proposed to manipulate the protein configuration by introducing TiO$_2$ nanoparticles in protein denaturation process, which results in a more opened-up protein configuration and more stable protein/TiO$_2$ structure.

(2) Introducing the more opened-up and more stable protein/TiO$_2$ nanoparticles into a PEO electrolyte significantly improves the electrolyte properties as compared with the relatively closed protein/TiO$_2$ nanoparticles. This is because the opened-up protein configuration helps to build faster ion-conduction pathways at the polymer-nanofiller interphases.

(3) Protein helps to dissociate lithium salts and therefore further facilitates the ion-conduction, because of the strong attraction force to anions coming from positively charged amino acids.

(4) 1 D protein/TiO$_2$ nanowires more effectively enhance the properties of the composite electrolytes, owing to their unique 1 D morphologies as compared with 0 D counterparts, which benefits formation of continuous ion-conduction pathways.

7.1.3 Protein-based binder for Li-S batteries

The protein-based binder in this study is demonstrated to show remarkable performances in mechanical properties, polysulfide-blocking function and ion-conduction ability. These good attributes all warrant the successful fabrication of high loading sulfur cathodes. Specific conclusions are shown below.

(1) Facile incorporation of protein and PAA leads to a network-structured protein-based binder with strong robustness, which helps to buffer the large volume change of sulfur.
(2) The rich functional groups of protein strongly bind polysulfides, significantly reducing the shuttle effect. Meanwhile, the ion-conduction ability of protein promotes the electrochemical reactions.

(3) The protein-based binder has abilities of improving electrode microstructures/mechanical properties, trapping polysulfides and facilitating ion-conduction, leading to good performance for high loading sulfur cathodes.

7.1.4 Protein nanofilter for Li-S batteries

Borrowing the concept from air filtration, a unique battery interlayer, i.e. protein nanofilter, for capturing polysulfides and facilitating transport of Li\(^+\) is developed. This study sets the basic requirements and design guidelines for advanced battery interlayers. Specific conclusions drawn from this study are listed below.

(1) The protein-direct self-assembly of conductive fillers leads to a unique porous structure of the resulting protein nanofilter, which is beneficial for reducing the cell resistance.

(2) The special configuration of the protein behaves like a “molecular cage” for accommodating polysulfides. Meanwhile, the polar functional groups of protein show strong interactions with polysulfides.

(3) An air pressure drop testing is viable for reflecting the ion-transport resistance brought from the interlayers.

(4) The design guidelines for advanced interlayers are proposed, including rational porous structure, good mechanical properties and functional surface properties for binding polysulfides.
7.2 Outlook

Utilization of proteins for energy storage applications has paved a new way for achieving advanced energy storage devices. The rich sources of protein and its intrinsic complexation in molecular compositions and structures, in spite of the challenge for uncovering them, indicate a vast variety of possibilities. The studies in this dissertation suggest that proteins, with a proper treatment or manipulation, can become unique and high-performance energy materials and show superior performance from nature. However, due to the complicated features of this whole system and our limited time, there are still some issues to be addressed. Future research directions are suggested as shown below.

(1) For protein-based solid electrolytes: The poor interfacial properties and relatively low ionic conductivity at room temperature are the two critical issues. The interfacial contact may be improved by directly depositing the protein-ion complex solution on the electrode surfaces and then removing the solvents. The ways for improving the ionic conductivity include but are not limited to changing denaturation conditions (solvents, temperature, etc.) and adding nanoparticles, polyelectrolytes or unique polymers for manipulating the protein configuration. Another critical challenge that may need to be addressed is the effects of protein on the formation of SEI layer.

(2) For composite electrolytes with protein/ceramic nanofillers: Searching for more effective nanofillers to be treated by protein represents a promising method to further improving the electrolyte properties. Instead of passive nanofillers, by combining ceramic ion conductors and protein may be beneficial for delivering higher ionic conductivity. Additionally, more polymer matrices are suggested to apply.

(3) For protein-based binder: Although the study in this dissertation has demonstrated that high loading sulfur cathodes are realized by the protein-based binder, the loading level needs to be
further elevated. Therefore, optimization of the binder compositions is needed, such as the blending polymers, the material ratios, etc. It is suggested that blending proteins with some special bio-polymers may further improve the mechanical properties and trapping ability for polysulfides, such as guar gum, xanthan gum, etc.

(4) For protein nanofilter: More types of conductive fillers are suggested to apply in addition to carbon black in the present study, e.g. carbon nanotubes, carbon nanofibers, etc. These conductive fillers exhibit different dimensions and may show improvement in the ability for trapping polysulfides. In addition, fabricating electrospun core-shell structured protein nanofilter is of great interests via applying protein as the shell and conductive nanofibers as the core.
REFERENCES


[109] L. Xing, K. Xi, Q. Li, Z. Su, C. Lai, X. Zhao, R. V. Kumar, J. Power Sources 2016, 303,
22.


115, 2718.


Interfaces 2018, 10, 4726.


1605531.


APPENDIX A

List of Author’s Publications


