DEVELOPMENT OF ADVANCED MATERIALS FOR NEXT GENERATION OF RECHARGEABLE BATTERIES

by

Xuemin Li
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Applied Chemistry).

Golden, Colorado

Date ________________________________

Signed: ________________________________

Xuemin Li

Golden, Colorado

Date ________________________________

Signed: ________________________________

Dr. Yongan Yang
Thesis Advisor

Golden, Colorado

Date ________________________________

Signed: ________________________________

Dr. David T. Wu
Professor and Head
Department of Chemistry
ABSTRACT

The increasing demands for next generation of rechargeable batteries evoke the development of advanced electrode materials. For my thesis, I mainly study two systems of lithium/sodium-containing electrode materials, that is, alkali sulfides (M₂S, M = Li and Na) cathodes and lithium silicides (LiₓSi) anodes.

We develop an innovative method of synthesizing anhydrous and morphology controllable M₂S nanocrystals (NCs) and demonstrate their potential as cathode materials for metal-sulfur batteries. Phase-pure M₂S-NCs are produced as precipitates during reactions between hydrogen sulfide (H₂S) and metalorganic complexes (R-M) in organic solutions. The reaction is thermodynamically favorable and enables tuning the M₂S-NC morphology via selecting different solvents and organic agents. In the ideal process, we have realized the net reaction of H₂S + 2M → M₂S + H₂, which integrates three desirable tasks: abating the hazardous H₂S, producing the wanted M₂S-NCs, and recovering valuable delivering hydrogen (H₂). All auxiliary reagents can be recycled directly without post-treatments. The electrode performance of synthesized Li₂S-NCs (~100 nm) is superior to that of commercial Li₂S micropowders in terms of capacity, cycling stability, output voltage, and voltage efficiency. This scalable approach provides an energy-efficient and environmentally-benign method to produce nanostructured cathode materials required in metal-sulfur batteries.

Among all candidates scrutinized for the anode, silicon (Si) is one of the most promising materials due to its high capacity. However, the existing studies of its lithiated counterpart – lithium silicide (LiₓSi) are limited. In this thesis, three thermodynamically-stable phases of LiₓSi (x = 4.4, 3.75, and 2.33) plus nitride-protected Li₄.₄Si synthesized via the high-energy ball milling technique are systematically studied. All three LiₓSi phases show better performance than Si, with Li₄.₄Si being the best. When a nitride shell (LiₓNₓSiₓ) is created on the surface of Li₄.₄Si, the cycling stability is significantly improved. Increasing nitridation extent can further improve the capacity retention, while the initial capacity decreases due to the inactivity of some Si in Li₄NₓSiₓ. Moreover, the Coulombic efficiencies of all LiₓSi-based electrodes of the first cycle are significantly higher than that of the Si electrode. Our study demonstrates the promises and challenges of developing lithium silicide anodes.
# TABLES OF CONTENTS

ABSTRACT ................................................................................................................................. iii

LIST OF FIGURES ...................................................................................................................... viii

LIST OF TABLES ......................................................................................................................... xiii

LIST OF ABBREVIATIONS ......................................................................................................... xiv

ACKNOWLEDGMENTS ............................................................................................................... xvi

CHAPTER 1 INTRODUCTION ..................................................................................................... 1

1.1 Background ......................................................................................................................... 1

1.1.1 Reactive Synthesis of Anhydrous M₂S Nanocrystals .................................................. 2

1.1.2 Lithium Silicide Nanoparticles as Anode Materials .................................................... 5

1.2 Thesis Organization ........................................................................................................... 8

1.3 References ......................................................................................................................... 9

CHAPTER 2 METHODOLOGY AND CHARACTERIZATION TECHNIQUES .............................. 17

2.1 Materials Synthesis Methodology ..................................................................................... 17

2.1.1 M₂S Synthesis ................................................................................................................ 17

2.1.2 LiₓSi Synthesis ................................................................................................................ 18

2.2 Characterization Techniques ............................................................................................ 18

2.2.1 Quadrupole Mass Spectrometry .................................................................................... 18

2.2.2 X-ray Diffraction .......................................................................................................... 19

2.2.3 Scanning Electron Microscopy ...................................................................................... 21

2.3 Battery Assembling and Performance Assessments ......................................................... 22

2.4 References ......................................................................................................................... 25

CHAPTER 3 THERMODYNAMICALLY FAVORABLE CONVERSION OF HYDROGEN SULFIDE INTO VALUABLE PRODUCTS THROUGH REACTION WITH SODIUM NAPHTHALENIDE ............................................................... 28

3.1 Abstract ............................................................................................................................. 28

3.2 Introduction ......................................................................................................................... 28

3.3 Results and Discussion ...................................................................................................... 30

3.4 Conclusion ........................................................................................................................ 35

3.5 Experimental Section ....................................................................................................... 36

3.5.1 Materials ....................................................................................................................... 36

3.5.2 Methods ......................................................................................................................... 36
5.5.1 Chemicals ........................................................................................................................... 64
5.5.2 Synthesis of Na$_2$S and Li$_2$S .......................................................................................... 65
5.5.3 Product Characterization ................................................................................................. 65
5.5.4 Hydrogen Quantification: ............................................................................................... 66
5.6 Results and Discussion ........................................................................................................... 66
  5.6.1 The Model Reaction – Synthesis of Na$_2$S Nanocrystals ................................................... 66
  5.6.2 H$_2$ Quantification .......................................................................................................... 68
  5.6.3 Speciation and Reuse of the Auxiliary Reagents ............................................................... 69
  5.6.4 Synthesis of Li$_2$S-NCs .................................................................................................. 70
  5.6.5 Morphology Control of Na$_2$S-NCs ................................................................................. 72
5.7 Conclusion ............................................................................................................................. 74
5.8 References .............................................................................................................................. 74
5.9 Supporting Information ......................................................................................................... 78

CHAPTER 6 STUDY OF LITHIUM SILICIDE NANOPARTICLES AS ANODE MATERIALS
FOR ADVANCED LITHIUM ION BATTERIES ........................................................................ 81
  6.1 Abstract ................................................................................................................................. 81
  6.2 Keywords ............................................................................................................................... 81
  6.3 Introduction ........................................................................................................................... 81
  6.4 Experimental Section .......................................................................................................... 83
    6.4.1 Chemicals and Materials ............................................................................................. 83
    6.4.2 Synthesis of Electrode Materials .................................................................................. 84
    6.4.3 Characterizations ......................................................................................................... 84
    6.4.4 Electrode Fabrication and Electrochemical Analysis ................................................... 85
  6.5 Results and Discussion ........................................................................................................ 85
    6.5.1 Characterization of Si, Li$_4$Si, and Li$_4$Si@Li$_x$N$_y$Si$_z$-1 ............................................. 85
    6.5.2 Electrode performance of Si, Li$_4$Si, and Li$_4$Si@Li$_x$N$_y$Si$_z$-1 .................................... 87
    6.5.3 The Effect of Nitridation Extent ................................................................................... 89
    6.5.4 The Effect of Electrode-Fabrication Procedure ......................................................... 90
    6.5.5 The Effect of Lithium Amount in Li$_x$Si (x = 3.75 and 2.33) .................................... 93
  6.6 Conclusions ........................................................................................................................ 95
  6.7 References ........................................................................................................................... 96
  6.8 Supporting Information ....................................................................................................... 100

CHAPTER 7 CONCLUSIONS AND FUTURE WORK ................................................................... 109
7.1 Conclusions ............................................................................................................................... 109
7.2 Future Work .............................................................................................................................. 110
7.3 References ............................................................................................................................... 111

APPENDIX A PERMISSIONS FOR USE OF CHAPTERS 3 AND 4 .................................................... 112
A.1 Background ............................................................................................................................... 112
A.2 Permissions ............................................................................................................................... 112
   A.2.1 Chapter 3 – ChemPlusChem, Wiley ................................................................................ 112
   A.2.2 Chapter 4 – ACS Applied Materials & Interfaces, American Chemical Society ............ 117
A.3 Email Correspondence from Coauthors .................................................................................... 120
   A.3.1 Email for Chapter 3 ........................................................................................................ 120
   A.3.2 Email for Chapter 4 ........................................................................................................ 121
LIST OF FIGURES AND SCHEMES

Figure 1.1 Schematic of a lithium ion battery with graphite anode and LiCoO2 cathode (copper current collector for the anode; aluminum current collector for the cathode; red dots for Li+). .......... 1
Figure 1.2 Scheme listing the current methods of producing M2S nanoparticles in research labs. .......... 4
Figure 1.3 The reaction strategy for M2S synthesis. .......................................................... 5
Figure 1.4 The scheme illustrating the fading mechanism of crystalline Si anode due to the pulverized Si and thickened SEI layer. Symbols “c-Si”, “Li,Si”, and “a-Si” refer to crystalline-silicon, lithium silicide, and amorphous-silicon, respectively. .......................................................... 6
Figure 1.5 Illustration of literature methods for accommodating the volume fluctuation for Si anodes. (A) Si@C core@shell composites; (B) crumpled-graphene-wrapped Si@C nanoparticles; (C) conformal Si@SiO2 double-walled nanotubes with inner void space; (D) Si@void@C core@void@shell composites; and (E) conductive polymer embedded Si nanoparticles. PANi and PPy refer to polyaniline and polypyrrole, respectively. ............................................. 7
Figure 1.6 Scheme highlighting the key creativity of our void-space-engineering strategy that produces high performance silicon anode by starting with Li4.4Si@ shell composites. .................. 8
Figure 2.1 Schematic of a quadrupole mass filter................................................................. 19
Figure 2.2 Schematic of the Bragg’s diffraction................................................................. 20
Figure 2.3 A typical CV figure showing the measurable parameters. ..................................... 24
Figure 2.4 Schematic of a typical Nyquist plot with the Randles equivalent circuit on the top. ........ 25
Figure 3.1 Demonstration of the proposed concept of removing H2S using Na-NAP. A) Real-time QMS measurements of the relative changes in H2S and H2 upon introduction of H2S to Na-NAP. B) Mass spectra showing that the 10% of H2S in Ar (black) is completely removed after treatment (red). C) XRD pattern (blue) and SEM image (inset) of the solid product and XRD stick pattern (black) of the Na2S standard......................................................... 31
Figure 3.2 Characterization of the organic compounds in the liquid phase. A) FTIR spectrum of the solid residue after removal of NAP and DME. B) 1H NMR spectrum of the liquid phase directly from the reaction system. ................................................................................... 32
Figure 3.3 GC–MS analysis of the liquid phase of the reaction system: (A) the chromatogram; (B) the MS spectrum for peak 1 in (A); and (C) the MS spectrum for peak 2 in (A)................................. 33
Figure 3.4 XRD data of solid products in three reactions using different Na-NAP/H2S molar ratios: 1.0 (A), 1.1 (B), and 3.4 (C). The standard XRD patterns (sticks) of the predominate chemicals are shown as references. ................................................................................................. 35
Figure 3.5 Photograph of the Na-NAP solution (A), schematic diagram (B) and photograph (C) of the reaction apparatus used for the proof-of-concept......................................................... 40
Figure 4.1 Characterization of the reaction for synthesizing Li2S nanocrystals. (A) Time evolution of QMS to monitor the concentrations of key species in the gas phase: argon (black); H2S (red); DME (blue). (B) MS spectra in the window of m/z 30–35 for the gaseous effluents through the bypass (black) and through the reactor (red). (C) XRD pattern of the obtained
solid product (red) together with the stick pattern (black) of the Li$_2$S standard (JCPDS 04-003-6927). (D) SEM image of the obtained solid product. .................................................................47

Figure 4.2 Characterization of the liquid phase collected from the synthetic reaction: (A) the $^1$H NMR spectrum; (B) the gas chromatogram; (C) MS spectrum for peak 1 in part B; (D) MS spectrum for peak 2 in part B. .................................................................................................................48

Figure 4.3 Characterization of s-Li$_2$S (red) after being dried at 250 °C for 20 h prior to electrochemical analyses, with c-Li$_2$S (blue) as reference: (A) TGA plots; (B) XRD patterns; (C) SEM image of s-Li$_2$S; (D) SEM image of c-Li$_2$S. .................................................................................................................49

Figure 4.4 Typical CVs in the first four cycles of s-Li$_2$S (A) and c-Li$_2$S (B), where the scan rate is 0.1 mV/s. .......................................................................................................................................51

Figure 4.5 Typical plots of specific capacity in charge (solid circles and squares) and discharge (open circles and squares) processes and coulombic efficiency (solid diamonds) versus cycle number for both s-Li$_2$S (red) and c-Li$_2$S (blue), for which the galvanostatic current is 116.6 mA/g (0.1 C, 1C = 1166 mA/g). .................................................................................................................51

Figure 4.6 Several cycles of voltage profiles against the specific capacity for s-Li$_2$S (A) and c-Li$_2$S (B), where the inset in (A) highlights the activation period in the first cycle. .................................................................53

Figure 4.7 Schematic diagram (A) and photograph (B) of the reaction apparatus used for synthesizing Li$_2$S..................................................................................................................................................59

Figure 4.8 XRD patterns (A and C) and SEM (B and D) characterization of the solid products out of two reactions that are conducted at the molar ratio of Li-NAP:H$_2$S = 3:1 (A and B) and 1.5:1 (C and D). .................................................................................................................................59

Figure 5.1 Proposed chemical pathway for the efficient and sustainable M$_2$S manufacturing. .................................................................63

Figure 5.2 Proof of the concept via the synthesis of Na$_2$S-NCs. (A) Schematic diagram of the reaction setup; (B) Time evolution of the QMS signals of Ar (black) and H$_2$S (red) in the gas phase; (C) Mass spectra in the m/z window of 30 – 35 for the gaseous effluents through the bypass (black) and through the reactor (red); (D) XRD pattern of the obtained solid product (red) with the standard Na$_2$S pattern (black, JCPDS 00-023-0441); (E) SEM images of the obtained solid product, with a higher magnification as the inset; (F) EDX spectrum of the obtained solid product, together with the atomic percentages of elements therein. ......................................................................................................................67

Figure 5.3 (A) TGA results for commercial Na$_2$S$\cdot$9H$_2$O (black) and two annealed Na$_2$S samples (red for s-Na$_2$S and blue for c-Na$_2$S); (B) XRD patterns of the annealed Na$_2$S powders (red for s-Na$_2$S and blue for c-Na$_2$S), with the Na$_2$S standard pattern (black, JCPDS 00-023-0441). .................................................................................................................................68

Figure 5.4 Hydrogen production and quantification from the reaction of Na with EtOH. (A) Mass spectrum of the gaseous effluent out of the reactor to show the production of hydrogen; (B) Hydrogen quantification by integrating the temporal H$_2$ flowrate (inset). .................................................................................................................................69

Figure 5.5 Demonstration of recycling the auxiliary reagents. $^1$H NMR spectra of (A) the EtOH/DME solution, (B) the EtONa-EtOH/DME solution, and (C) the supernatant collected from the synthetic reaction. The insets in (A), (B), and (C) highlight the $^1$H peaks from -CH$_3$ in EtOH. (D) Time evolution of QMS of Ar (black) and H$_2$S (red) in the gas phase during the 2nd round of reaction using the recycled reagents. (E) The corresponding mass spectra in the m/z window of 30 – 35 for the gaseous effluents through the bypass (black) and
through the reactor (red). (F) The corresponding XRD pattern of the obtained solid product (red) with the standard Na$_2$S pattern (black, JCPDS 00-023-0441). ............................................. 70

Figure 5.6 XRD patterns (A-C) and SEM images (D-F) of Li$_2$S products from using different solvents: DBE (A and D), toluene (B and E), and hexane (C and F). The stick patterns in A – C are for the Li$_2$S reference (JCPDS: 04-003-6927). ................................................................. 72

Figure 5.7 Na$_2$S morphology tuning by changing alcohols and solvents. SEM images of the obtained solid products from the reactions of H$_2$S with sodium ethoxide (A-C) or sodium butoxide (D-F) in the solvents of DME (A and D), 2-MeTHF (B and E) or dioxane (C and F). .......... 73

Figure 5.8 (A) H$_2$ calibration curve of H$_2$ flow rate versus QMS intensity ratio of H$_2$/Ar (AMU2/AMU40); (B) Real time QMS intensity ratio of H$_2$/Ar in the reactor……………….. 78

Figure 5.9 Characterizations for the reaction of H$_2$S with EtOLi-EtOH/DME. (A) Time evolution of QMS for Ar (black) and H$_2$S (red); (B) Mass spectra in the m/z window of 30 – 35 for the gaseous effluents through the bypass (black) and the reactor (red); (C) XRD patterns of the obtained solid product (red) from the reaction and synthesized EtOLi powder (blue) with the standard pattern of Li$_2$S (black, JCPDS: 04-003-6927); (D) SEM images of the obtained solid products………………………………… 79

Figure 5.10 XRD results of the produced solid powders from the reactions of H$_2$S with EtOLi in 2-MeTHF (A) and dioxane (B)................................................................. 79

Figure 5.11 XRD results of the synthesized Na$_2$S from the reactions of H$_2$S with EtONa (A-C) and BuONa (D-F) in the solvents of DME (A and D), 2-MeTHF (B and E) or dioxane (C and F)…………………………………………………………………………………………………… 80

Figure 5.12 XRD results of the solid products from the reactions of H$_2$S with EtONa in DBE (A), toluene (B) and hexane (C).…………………………………………………………………… 80

Figure 6.1 XRD patterns (A - C) and SEM images (D - F) of three electrode materials: Si (A and D), Li$_{4.4}$Si (B and E), and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (C and F). ............................................................................................... 86

Figure 6.2 S/TEM of Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 samples: High-angle annular dark field (HAADF) STEM imaging (A and B), bright-field STEM imaging (C and D), and bright-field TEM imaging (E and F). Scale bars in A – D are all 500 nm and scale bars in E – F are both 20 nm. .......................................................................................................... 88

Figure 6.3 Plots of specific capacity (A), capacity retention (B), and Coulombic efficiency (C) against the cycle number for three electrodes made from Si (black), Li$_{4.4}$Si (blue), and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (red). The charging capacity (solid symbols) and the discharging capacity (open symbols) are calculated versus the mass of silicon and measured with the galvanostatic current of 358 mA/g-Si (0.1 C, 1C = 3580 mA/g-Si). ................................................................................................... 90

Figure 6.4 Investigation of the nitridation effect. (A) XRD patterns of Li$_{4.4}$Si (black), Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (red), Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-2 (blue), Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-3 (magenta), and commercial Li$_3$N (green). (B) The region of 38˚ - 48˚ in (A) to highlight the position shift of the strongest diffraction peak. (C) Plots of the specific capacity in the charging capacity (solid symbols) and the discharging capacity (open symbols) against the cycle number for three different Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$ samples. (D) The corresponding plots of capacity retention with respect to (C). ........................................................................................................... 90

Figure 6.5 Plots of specific capacity (A), capacity retention (B), and Coulombic efficiency (C) against the cycle number to compare the performance of Si, Li$_{4.4}$Si and Li$_{4.4}$Si@
Li_N_y_Si_z-1 electrodes prepared by ball milling the mixture of 64% active materials, 28% AB and 8% PVDF. .......................................................... 91

Figure 6.6 Voltage profiles (A – C) and CV plots (D – F) at the scan rate of 0.1 mV/s for electrodes of Si (A and D), Li_4.4Si (B and E), and Li_4.4Si@Li_N_y_Si_z-1 (C and F) .................................................. 92

Figure 6.7 The experimental EIS spectra (blue) and the fitting lines (red) for three materials: Si (A), Li_4.4Si (B), and Li_4.4Si@Li_N_y_Si_z-1 (C) at open circuit potential; the equivalent circuit models are listed above each specific figure. ......................................................... 93

Figure 6.8 Plots of the specific capacity against the cycle number to compare the performance of Li_4.4Si, Li_3.75Si and Li_2.33Si with delithiation first (A) and lithiation first (B). ........................ 94

Figure 6.9 CV plots for Li_3.75Si (A and B) and Li_2.33Si (C and D) with delithiation first (A and C) and lithiation first (B and D). .......................................................................................... 95

Figure 6.10 Characterizations of commercial Si micropowder by XRD (A), EDS (B), and SEM (the inset in B) ........................................................................................................... 100

Figure 6.11 Representative STEM images of Li_4.4Si and Li_4.4Si@Li_N_y_Si_z-1 with numbered boxes indicating areas where EDS measurements shown in Table 6.1 were quantified. ........ 101

Figure 6.12 EDS elemental mapping of Li_4.4Si. (A) HAADF image showing the area measured; (B) Si mapping; (C) N mapping; (D) O mapping; (E) Overlay of Si and N; (F) Overlay of HAAD image and Si signal; (G) Overlay of HAAD image and N signal; and (H) Overlay of HAAD image and O signal. ......................................................... 102

Figure 6.13 EDS elemental mapping of Li_4.4Si@Li_N_y_Si_z-1. (A) HAADF image showing the area measured; (B) Si mapping; (C) N mapping; (D) O mapping; (E) Overlay of Si and N; (F) Overlay of HAAD image and Si signal; (G) Overlay of HAAD image and N signal; and (H) Overlay of HAAD image and O signal. ......................................................... 103

Figure 6.14 FFT analysis from HRTEM of the amorphous edge layer (blue solid lines) and inner crystalline material (red dashed lines) of Li_4.4Si@Li_N_y_Si_z-1. ........................................... 103

Figure 6.15 EDS spectra of Si (A), Li_4.4Si (B), and Li_4.4Si@Li_N_y_Si_z-1 (C) with the wt% and at% of the respective elements and the molar ratio of N/Si. These data were obtained when taking the SEM images in Figure 6.1 ................................................................. 103

Figure 6.16 Cycle performance (A) and Coulombic efficiency (B) of electrodes using commercial Si materials. In each figure, the conditions used to prepare the electrode mixture are compared, non-ball milled 80 wt% active materials with 12 wt% AB, and 8 wt% PVDF (black) and ball milled 64 wt% active materials with 28 wt% AB and 8 wt% PVDF (red). .................. 104

Figure 6.17 Plots of specific charging capacity (solid symbols) and discharging capacity (open symbols) against the cycle number for Li_4.4Si@Li_N_y_Si_z-3. ......................................................... 105

Figure 6.18 SEM (C and D) and EDS (A and B) characterizations of Li_4.4Si@Li_N_y_Si_z-2 (A and C) and Li_4.4Si@Li_N_y_Si_z-3 (B and D). ................................................................. 105

Figure 6.19 Comparison of the cycling performance of Li_4.4Si (A) and Li_4.4Si@Li_N_y_Si_z-1 (B) electrodes made by three different processes: (black) no ball milling, 80 wt% active materials with 12 wt% AB, and 8 wt% PVDF; (blue) ball milled, 80 wt% active materials with 12 wt% AB, and 8 wt% PVDF; (red) ball milled, 64 wt% active materials with 28 wt% AB and 8 wt% PVDF. ................................................................. 106
Figure 6.20 The electrochemical analysis of electrode prepared from untreated commercial Si micropowder (ball milled 64 wt% active material with 28 wt% AB and 8 wt% PVDF). (A) voltage profiles; (B) dQ/dV plots; (C) CV results; and (D) EIS spectrum.

Figure 6.21 The dQ/dV plots for electrodes of Si (A), Li$_{4.4}$Si (B) and Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ (C).

Figure 6.22 XRD results (A and B) and SEM images (C and D) of Li$_{3.75}$Si (A and C) and Li$_{2.33}$Si (B and D).

Figure 6.23 SEM images to study the possible morphological changes of Li$_{3.75}$Si and Li$_{2.33}$Si after the initial lithiation or delithiation. Pristine synthesized Li$_{3.75}$Si (A); DEC cleaned anode of Li$_{3.75}$Si after the first half cycle of delithiation (B), and that after the first half cycle of lithiation (C); pristine synthesized Li$_{2.33}$Si (D); DEC cleaned anode of Li$_{2.33}$Si after the first half cycle of delithiation (E), and that after the first half cycle of lithiation (F).

Scheme 3.1 The proposed reaction mechanism of removing H$_2$S with Na-NAP to produce 1,4-dihydronaphthalene through a radical hydrogenation reaction. Intermediates: An NAP molecule (1) receives an electron from Na; an NAP$^-$ radical (2), a hydrogenated NAP$^-$ radical (3), a hydrogenated NAP anion (4), and a 1,4-dihydronaphthalene molecule (5).
LIST OF TABLES

Table 5.1 Factors that may affect the M₂S morphology .................................................................74
Table 5.2 The solubility of Na₂S and Li₂S in alcohols ..................................................................80
Table 6.1 Normalized quantification, averages, and standard deviations of silicon and nitrogen content from EDS measurements, as indicated in Figure 6.11. Oxygen (from air exposure of sample), carbon (from support film), and iron (from ball milling) are omitted….101
Table 6.2 Comparison of various studies of Li₅Si for battery applications .................................104
LIST OF ABBREVIATIONS

Lithium ion battery ............................................................... LIB
Hydrogen sulfide................................................................. H$_2$S
Naphthalene ............................................................... NAP
Sodium naphthalenide ........................................................ Na-NAP
Lithium naphthalenide ........................................................ Li-NAP
Alkali metal ................................................................. M
Sodium .................................................................................. Na
Lithium ................................................................. Li
Argon .................................................................................. Ar
Sulfur .................................................................................. S
Alkali metal sulfide ............................................................... M$_2$S
Lithium sulfide ................................................................. Li$_2$S
Sodium sulfide ................................................................. Na$_2$S
Ethanol ............................................................................. EtOH
Sodium ethoxide .............................................................. NaOEt
Lithium ethoxide ............................................................... LiOEt
Hydrogen ......................................................................... H$_2$
1,2-dimethoxyethane ......................................................... DME
Amorphous ................................................................. a
Crystalline .......................................................................... c
Carbon ................................................................................ C
Silicon ............................................................................... Si
Lithium silicide .................................................................. Li,Si
Nitrogen ......................................................................... N
Solid electrolyte interface ................................................ SEI
Copper ............................................................................ Cu
Lithium .............................................................................. Li
Ethylene carbonate .......................................................... EC
Diethyl carbonate ............................................................. DEC
Acetylene black ................................................................... AB
<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylidene fluoride</td>
<td>PVDF</td>
</tr>
<tr>
<td>Lithium hexafluorophosphate</td>
<td>LiPF&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>Nanocrystals</td>
<td>NCs</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>NPs</td>
</tr>
<tr>
<td>Nanometer</td>
<td>nm</td>
</tr>
<tr>
<td>Micrometer</td>
<td>µm</td>
</tr>
<tr>
<td>Volt</td>
<td>V</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>XRD</td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>SEM</td>
</tr>
<tr>
<td>Transmission electron microscopy</td>
<td>TEM</td>
</tr>
<tr>
<td>Energy dispersive X-ray spectroscopy</td>
<td>EDS</td>
</tr>
<tr>
<td>Cyclic Voltammetry</td>
<td>CV</td>
</tr>
<tr>
<td>Electrochemical impedance spectroscopy</td>
<td>EIS</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

Thank you to everyone that has helped me along the way. With special thanks to:

My advisor Dr. Yongan Yang

The Yang Group:
The graduate students: Yangzhi Zhao
The graduate alumni: Jake Bell, Dr. Jacqui Cloud, Dr. Tara Yoder
The postdoctors/visiting professors: Dr. Jie Qu, Dr. Yonglong Wang
The undergraduate students: Grace Anderson, Alice Brenna, Lauren Cain, Reed Hendrickson,
Kristen Hietala, John Ke, Faith Kersey-Bronce, Miranda McCeig, Julianna Richie, Joshua Schechter

Dr. Chunmei Ban and Dr. Robert Tenent at National Renewable Energy Laboratory

My committee members:
Dr. Collin A. Wolden (committee chair), Dr. Ryan Richards, Dr. Kim Williams

Additional support from:
Dr. Katie Hurst, Dr. Seoung-Bum Son, Dr. Yuan Yang, Edward Dempsey

Thank you to my family for all the amazing support and love over the years.

My funding sources:
Dr. Yongan Yang’s Startup Fund from the Colorado School of Mines (CSM)
Colorado Office of Economic Development and International Trade (COEDIT)
Renewable Energy Materials Research Science and Engineering Center (REMRSEC)
Teaching Assistantships from the Department of Chemistry at CSM
Vehicles Technologies Office,
CHAPTER 1
INTRODUCTION

1.1 Background

On one hand, conventional fuel deployment based on petrochemicals has played a pivotal role in meeting the global energy electricity demands; on the other hand, it also causes several critical issues, such as energy crisis, air pollution, acid precipitation, and ozone depletion, etc. It is predicted that, with the continuous increase of global population, the global energy demand will increase by an order of magnitude by 2050.\(^1\) Renewable energy development (such as solar, wind, and biomass energy) has the potential to be sustainable and reduce the dependence on conventional fuels. However, some renewable energy sources, such as solar and wind energy, are intermittent and require advanced energy storage technologies.\(^2\)

One critical energy storage technology is rechargeable batteries. Currently, the most advanced rechargeable batteries are lithium ion batteries (LIBs), superior to many conventional secondary batteries like nickel–cadmium (Ni–Cd), nickel-metal hydride (Ni-MH), and lead acid battery systems, because they possess the properties of higher volumetric and gravimetric energy storage capability, no memory effect, and very low self-discharge.\(^3\) An LIB has mainly four components: an anode, a cathode, an electrolyte solution, and a separator, shown in Figure 1.1.\(^4\) During the charging process, energy is stored inside when lithium ions (Li\(^+\)) and electrons are extracted out of the cathode and injected into the anode. During the discharging process, energy is released to the external circuit, when Li\(^+\) ions and electrons are extracted from the anode to the cathode.

![Figure 1.1 Schematic of a lithium ion battery with graphite anode and LiCoO\(_2\) cathode (copper current collector for the anode; aluminum current collector for the cathode; red dots for Li\(^+\)).](image-url)
LIBs have been widely used in portable electronic devices, such as notebook computers, mobile phones, hybrid vehicles and electric vehicles. Nevertheless, the current generation of LIBs has reached the limit of their practically-achievable performance.\(^5-7\) The sole anode material of graphite and the prevailingly used cathode material of lithium metal oxide (LMO) have layered structures and store lithium ions in their interlayer void space, which are called intercalation type materials. During the lithium insertion and extraction, their crystal structures do not change, yet with small volume changes.\(^7\) In spite of the structural stability, the intercalation-based batteries suffer from low capacity (the quantity of Li\(^+\) ions stored per unit of mass or volume) and low energy density (the amount of energy stored per unit of mass or volume). To meet the need for large scale of energy storage in electric vehicles and grid energy storage, the development of advanced electrode materials for next generation LIBs is imperative.

Beyond the intercalation type materials, two new kinds of techniques under the extensive development are alloying type materials and conversion type materials.\(^8\) In the alloying type materials, such as silicon (Si), germanium (Ge), and tin (Sn), the electrode material alloys with lithium to form a homogeneous solid solution of Li\(_x\)Si, Li\(_x\)Ge, and Li\(_x\)Sn. In the conversion type materials, the electrode material goes through drastic structural change after lithiation and delithiation, which requires breaking and reforming bonds.\(^9, 10\) For example, the conversion reactions for FeS\(_2\) cathode during the fully discharging and charging processes can be expressed as Reaction 1.1 and Reaction 1.2, respectively.\(^11, 12\)

\[
\text{Discharging process: } 4\text{Li}^+ + 4e^- + \text{FeS}_2 \rightarrow 2\text{Li}_2\text{S} + \text{Fe} \quad (1.1)
\]

\[
\text{Charging process: } 2\text{Li}_2\text{S} + \text{Fe} - 4e^- \rightarrow 4\text{Li}^+ + (2-y)\text{S} + \text{FeS}_y \quad (1.2)
\]

These two mechanisms offer higher specific capacity and energy density compared with the intercalation mechanism.\(^10, 13\) Among many scrutinized materials, Si is one of the most promising anode materials,\(^14\) and anhydrous alkali sulfide (M\(_2\)S, M = Li and Na) nanocrystals (NCs) are important materials central to the development of next generation cathodes and solid state electrolytes for advanced batteries.\(^9, 15\) Thus, my thesis research focuses on developing Li/Na-containing cathodes (M\(_2\)S) and anodes (Li\(_x\)Si, lithium silicide), which will be elaborated below.

### 1.1.1 Reactive Synthesis of Anhydrous M\(_2\)S Nanocrystals

In past decades, great efforts have been invested on metal-sulfur (M–S) batteries due to the advantages of high theoretical energy and high earth abundance of the sulfur cathode.\(^4, 15-17\) However, during cycling, harmful dendrite structures form on the metal anode, which can grow and penetrate the separator, causing serious problems of short-circuit, thermal runaway, and even fire.\(^18\) Another issue of S is the large volume fluctuation (as high as 80\%) caused by the charging/discharging steps.\(^19-22\) To solve the
problem, one strategy widely studied is to use M$_2$S as the alternative cathode material because M$_2$S avoids the development of metal anodes and enables pairing with current or emerging non-metal anodes, such as graphite or silicon.\textsuperscript{23} Moreover, M$_2$S does not require preset void space for accommodating the volume fluctuations. In principle, when Li$_2$S/Na$_2$S goes through the initial electrochemical delithiation/desodiation process, an adequate volume of void space around every particle can be created to accommodate the subsequent lithiation/sodiation processes. Also, due to the higher melting/boiling points, M$_2$S has greater thermal stability and permits a wider temperature window for electrode fabrications.\textsuperscript{24} Li$_2$S cathode is used in lithium ion batteries, and Na$_2$S cathode is used in sodium ion batteries. Sodium ion batteries (SIBs), with a similar working principle as LIBs, are considered promising renewable energy storage alternatives because of the abundance and low cost of Na.\textsuperscript{25} Recently, Na$_2$S cathode has been extensively studied for room temperature Na-S batteries.\textsuperscript{26, 27}

M$_2$S NCs are also key materials for all-solid-state lithium or sodium ion batteries which use safer inorganic solid electrolytes. Owing to high conductivity and ductility,\textsuperscript{28, 29} sulfide ceramics, derived from lithium/sodium sulfides such as the leading candidates based on the Li$_2$S-P$_2$S$_5$,\textsuperscript{30} Na$_2$S-P$_2$S$_5$,\textsuperscript{31} Na$_2$S-GeS$_2$,\textsuperscript{32} and Li$_2$S-GeS$_2$\textsuperscript{33} systems, are prominent solid electrolyte materials for all-solid-state batteries. In addition, sulfides can even be used in both electrodes and solid electrolytes. For example, a single-material battery is built using Li$_{10}$GeP$_2$S$_{12}$ as the electrolyte, anode, and cathode based on the fact that two pairs of redox reactions occur when the material is scanned at low and high voltage windows.\textsuperscript{33} One pair of reversible redox peaks at the low potential (0.0–0.5 V) is observed, and another pair of reversible redox peaks at the high potential (1.6–2.7 V) is observed.\textsuperscript{33} In the composite of Li$_{10}$GeP$_2$S$_{12}$, Li–S and Ge–S components behave as the cathode and anode active centers, respectively.\textsuperscript{33} These advantages boost the ever-increasing global interest of developing M$_2$S materials.

However, there are challenges for M$_2$S synthesis. The commercial synthesis is usually energy intensive and cost ineffective. Reactions from 1.3 to 1.6 list the current M$_2$S preparation methods.\textsuperscript{34-37} The first approach (Reaction 1.3), although thermodynamically favorable, requires high temperature to activate the reaction. In the second thermodynamically unfavorable approach (Reaction 1.4), the products of M$_2$S and H$_2$O are not compatible with each other, resulting in high separation costs. For the third and fourth reactions (Reactions 1.5 and 1.6), in addition to the disadvantage of high separation cost, the carbon dioxide emission is not environmentally friendly. Furthermore, nanostructured M$_2$S materials are commercially unavailable from all these methods because high temperature is used in the synthesis techniques.\textsuperscript{23, 37, 38} Compared with micro particles, reducing the electrode and solid electrolyte particle size is very valuable in improving the interfacial contacts among active materials, carbon black and solid electrolyte. Thus, the
ionic conductivity of the electrode is improved. That is why new synthesis methods for M$_2$S NCs need to be developed.

\[
2\text{M(l)} + \frac{1}{8}\text{S}_8 \xrightarrow{T\geq300\,^\circ\text{C}} \text{M}_2\text{S(s)} \quad \Delta G_m^0 \approx -380\,\text{kJ/mol} \quad (1.3)
\]

\[
2\text{MOH (s)} + \text{H}_2\text{S(g)} \xrightarrow{T=130-445\,^\circ\text{C}} \text{M}_2\text{S(s)} + \text{H}_2\text{O(g)} \quad \Delta G_m^0 \approx +200\,\text{kJ/mol} \quad (1.4)
\]

\[
\text{M}_2\text{SO}_4(s) + 2\text{C (s)} \xrightarrow{T=600-1000\,^\circ\text{C}} \text{M}_2\text{S(s)} + 2\text{CO}_2(g) \quad \Delta G_m^0 \approx +120\,\text{kJ/mol} \quad (1.5)
\]

\[
\text{M}_2\text{CO}_3(s) + \text{H}_2\text{S(g)} \xrightarrow{T=500-700\,^\circ\text{C}} \text{M}_2\text{S(s)} + \text{H}_2\text{O(g)} + \text{CO}_2(g) \quad \Delta G_m^0 \approx +100\,\text{kJ/mol} \quad (1.6)
\]

M$_2$S nanoparticles have been synthesized in research labs via different ways, shown in Figure 1.2. These methods mainly include ball milling micro-sized M$_2$S (Figure 1.2A), recrystallization of dissolved M$_2$S micropowders (Figure 1.2B), electrochemical or chemical lithiation/sodiation of premade S nanoparticles (Figure 1.2C), and conventional carbothermal reduction (Figure 1.2D). In the ball milling method, the product size distribution is broad. The recrystallization method is time consuming because a large amount of the solvents need to be evaporated at a given temperature close to the boiling point of the solvents. The third method is also time consuming and requires premade S nanoparticles for the synthesis. The fourth method, similar as one of the industrial methods (Reaction 1.5), needs very high temperature (820 – 900 °C) for more than 2 hours. Generally, these approaches are energy intensive and difficult for commercial scale production. To solve the problem, we aim to synthesize high performance M$_2$S NCs for next generation rechargeable batteries, using an energy efficient and cost effective method.

![Figure 1.2 Scheme listing the current methods of producing M$_2$S nanoparticles in research labs.](image)

Our synthesis strategy is to react hydrogen sulfide (H$_2$S) gas with a metalorganic reagent in an organic solvent (as shown in Figure 1.3 on page 5), which is a thermodynamically favorable reaction due
to its very negative $\Delta G_m^{\circ}$. The solid $M_2S$ products can be separated very easily from the reaction solution through centrifugation. In the ideal case, the organic solution can be recycled to replenish the metalorganic solution and co-generate hydrogen gas ($H_2$) by reacting with metal ($M$). Consequently, the net reaction of the designed technology is the reaction of $M$ with $H_2S$ to produce $M_2S$ and $H_2$ at room temperature.

Figure 1.3 The reaction strategy for $M_2S$ synthesis.

The novelty of our technique can be summarized as follows. First, it does not require high temperatures, due to the favorable thermodynamics, which enables the reaction to rapidly proceed to completion at the ambient temperature and normal pressure. Second, the product separation is simple and easy because the $H_2$-recovery is decoupled from the $H_2S$-consumption and in both steps different chemicals exist in different phases. Third, the liquid auxiliary reagents can be easily recollected and directly recycled to enable a continuous process for industrial manufacturing. Fourth, the value of $M_2S$ is many times higher than that of $M$, which can significantly offset the costs. Fifth, this technique completely consumes $H_2S$, a major industrial pollutant that is generated worldwide at the level of 70 million tons/year and must be reduced to $\sim 10$ ppm before air emission. Thus, it is expected that the $H_2S$-generating industries (such as petroleum refinery, natural gas, paper production, etc.) would welcome this technique. Sixth, $H_2$ is a high value chemical, which is mainly derived from stream reforming of fossil fuels through energy intensive processes, requiring extensive separation and purification. So, recovering high purity $H_2$ from an industrial waste at room temperature is a significant benefit. Thus, this scalable, energy efficient, and economically-sound technology is potentially transformative.

The goal of this project is to develop a practically-scalable method of producing high-performance $M_2S$ NCs with different morphologies for advanced rechargeable batteries. Details are included in Chapter 3-5 about synthesizing $M_2S$ NCs, tuning the particle morphology, and comparing the electrode performance of the synthesized $M_2S$ with commercial $M_2S$ materials.

### 1.1.2 Lithium Silicide Nanoparticles as Anode Materials

Si has been extensively studied and considered as the most promising anode material because of its high charge capacity (4200mAh/g), earth abundance, low cost, and long history of well-developed
However, very poor cyclability of Si due to large volume fluctuation during the charging/discharging cycles inhibits its commercialization. Figure 1.4 conceptually illustrates the poor cyclability of a thin film crystalline Si (c-Si). The initial lithiation (step 1) of c-Si (i) to generate Li$_x$Si (ii) causes huge volume expansion (300%). Meanwhile, a protective layer of solid electrolyte interphase (SEI) is formed on the Li$_x$Si surface due to the reduction of the electrolyte by Li$_x$Si (ii). The subsequent delithiation (step 2), converting Li$_x$Si to amorphous Si, causes the material to shrink. Therefore, the resulting stress cracks the Si electrode and the SEI layer (iii). After multiple cycles of lithiation/delithiation (step 3), the electrode materials are pulverized, and lose electrical contact with the current collector. In addition, the SEI layer repeatedly grows on the newly-exposed surface of the pulverized Si electrode, impeding Li$^+$ ions transferring to Si and consuming more and more electrolyte and Li$^+$ ions. Finally, the battery dies with poor cyclability.

Figure 1.4 The scheme illustrating the fading mechanism of crystalline Si anode due to the pulverized Si and thickened SEI layer. Symbols “c-Si”, “Li$_x$Si”, and “a-Si” refer to crystalline-silicon, lithium silicide, and amorphous-silicon, respectively.

In order to mitigate the problem, great efforts have been made to accommodate the volume fluctuation, such as designing composite nanostructures, exploring new binders, and limiting charging/discharging voltages. To date, many researchers have designed and synthesized new composite materials (shown as Figure 1.5 on page 7) and have achieved significant performance improvement. The frequently demonstrated approach is to coat Si nanoparticles with carbon (C) shells (Figure 1.5A). However, the composite materials still suffer from serious damage during lithiation/delithiation because of cracking or insufficient coverage of the C shell. The general idea of another method (Figure 1.5B-D) is to create void space for Si particles, which has proven effective to improve battery performance. For example, wrapping Si nanoparticles inside of crumpled graphene nanosheets (Figure 1.5B), creates some void space among Si particles. Another example (Figure 1.5C) is to fabricate Si@SiO$_2$ double-walled nanotubes to build up inner void space so that during the Li$^+$ insertion, the material mainly expand inward with limited outer expansion due to the limitation of the rigid SiO$_2$ out layer. An alternative (Figure 1.5D) is to synthesize Si@void@C core@void@shell nanoparticles, which can be realized by removing the SiO$_2$ sacrificial layer from the Si@SiO$_2$@C composite using the hydrofluoric acid (HF) treatment. In addition, people also embed Si nanoparticles in an elastic, porous, and conductive polymer matrix, which is helpful to accommodate the volume fluctuation, shown as Figure 1.5.
However, these approaches still have shortcomings, such as incomplete seal in the core@shell structures, imperfect void space for each Si particle, and difficulty in controlling the space among Si particles. Hence, it is necessary to develop alternative methods to solve the problem.

We hypothesize that fully lithiated nanoparticles (lithium silicide, $\text{Li}_x\text{Si}$) with the protection from a conductive and robust shell (such as C) can create perfect void space for every Si particle regardless of the particle size, shape, location, and loading amount, illustrated by Figure 1.6 (page 8). The novelty is that after the initial electrochemical delithiation, the void space between the amorphous Si and the shell for every particle will perfectly accommodate the volume expansion in the subsequent lithiation (step 1). It is also assumed that this situation should be true for the following cycles (steps 2 and 3). As a result, no particles become compressed or displaced by their neighboring particles and no macroscopic volume-change is involved. These features will greatly ease the electrode fabrication and are highly desirable compared with the difficulty of presetting perfect void space (or the porosity) in conventional approaches. After many cycles (step 3), the electrode is expected to maintain good electrical contact with the current collector and contains a stable SEI layer. Hence, the volume-fluctuation induced electrode damage will be minimized. Moreover, lithium silicides have better conductivity, and it can be paired with non-lithiated cathodes like sulfur, a cathode in the course of exploded studies in the past decade.\textsuperscript{18, 71-74} With such attractive features, $\text{Li}_x\text{Si}$ electrodes deserve a systematic exploration for the development of anode materials.
Compared with Si, the existing studies on Li$_x$Si are very limited. In the literature, the Li$_x$Si electrodes are primarily amorphous Li$_x$Si, synthesized by electrochemical lithiation of Si in a temporary battery,\textsuperscript{75, 76} or chemical lithiation through contacting Si with lithium metal or lithium compounds.\textsuperscript{76-78} There are a couple of methods to make Li$_x$Si crystals.\textsuperscript{79-82} The first method is thermochemical synthesis by reacting Li metal with Si powder at elevated temperatures.\textsuperscript{80} The second method is mechanochemical synthesis by milling Li metal and Si powder in a ball mixing apparatus.\textsuperscript{81, 83} However, the performance achieved so far on the crystalline Li$_x$Si is poor and there are no systematic studies on different Li$_x$Si phases.\textsuperscript{84, 85} Therefore, systematic study of Li$_x$Si phases are of great significance to better understand their promises and challenges.

However, Li$_x$Si anode remains challenging because of its high reactivity.\textsuperscript{79} Thus, the surface of Li$_x$Si needs to be protected before building the targeted conductive and robust shell. Learning from the fact that Li can readily react with nitrogen (N\textsubscript{2}) gas at room temperature to form lithium nitride (Li$_3$N),\textsuperscript{86, 87} we hypothesize that Li$_{4.4}$Si can react with N\textsubscript{2} to generate a nitride layer outside its surface. The synthesis of the protecting layer is expected to be easy, cost effective and energy efficient. Li$_3$N is thermally robust, chemically stable and mechanically strong.\textsuperscript{88-90} Particularly, it is also a superionic Li-ion conductor, comparable with many organic liquid electrolytes.\textsuperscript{91} Nitrogen atoms are assumed to react only with the surface material without entering the bulk, because the diffusion coefficient of nitrogen is as low as 3.66×10$^{-15}$ cm$^2$s$^{-1}$ in silicon.\textsuperscript{92} Due to the presence of Si, the nitride layer is expected not to exist as pure Li$_3$N and better denoted as Li$_x$N$_y$Si$_z$. The nitridation may result in Li$_x$Si-based electrode materials with improved cyclability and provide a promising surface-protection method for the subsequent fabrication of the conductive and robust shell.

The goal of this research project is to develop high-performance Li$_x$Si electrodes. The first objective is to synthesize pure Li$_x$Si (x = 4.4, 3.75, and 2.33) and compare their electrode performances. Then the surface-nitridated structure of Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$ is built and its electrode performance is compared with Li$_{4.4}$Si.

1.2 Thesis Organization

This thesis is organized into seven chapters for two research projects. Chapter 1 is the background information and literature results for the following chapters. Chapter 2 includes the characterization
information and the basic principle for some instrumentation techniques frequently used in the thesis such as quadrupole mass spectrometry (QMS), X-ray diffraction (XRD), and scanning electron microscope (SEM). The characterizations of synthesized products are crucial for analyzing and understanding the research, developing research plan and distributing the scientific knowledge. In addition, Chapter 2 also includes the information about the electrode performance assessments for the synthesized materials and electrochemical analysis including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to understand the redox reactions in the battery.

Chapter 3, 4, and 5 provide comprehensive and detailed research results about the M₂S project. Chapters 3 and 4 are about the first version of M₂S synthesis. Specifically, Chapter 3 is a work published in ChemPlusChem and focuses on the proof of concept of our synthesis method for the Na₂S nanoparticles synthesis using metal naphthalenide complex as the organic reagent. Chapter 4 is a paper published in ACS Materials and Interfaces, which systematically studies Li₂S NCs synthesized using the naphthalenide strategy. In this chapter, the electrode performance is studied using the synthesized Li₂S NCs which show superior performance compared with the commercial Li₂S materials. Chapter 5 is for the second version of M₂S synthesis, demonstrating the success of realizing the ideal process shown in Figure 1.3 (page 5). This chapter has detailed research information about synthesis of M₂S NCs using metal alkoxide complex as the organic reagent, complete hydrogen production, recyclization of the auxiliary reagents, and morphology tuning for M₂S NCs.

Chapters 6 is about the second project of lithium silicide, with detailed experimental design and research results. Synthesis of different lithium silicides and their electrode performance are included. Moreover, nitrogen treatment for the lithium silicide is beneficial to protect the active material and to improve the cycling stability.

Finally, Chapter 7 is the general conclusions and future work for two projects. This chapter provides a comprehensive summary of the successes and significance of this thesis, together with a perspective outlook of future directions.

1.3 References


(47) Zhou, H., Wang, X., and Chen, D., "Li-Metal-Free Prelithiation of Si-Based Negative Electrodes for Full Li-Ion Batteries". *ChemSusChem 2015, 8(16), 2737-2744*.


CHAPTER 2
METHODOLOGY AND CHARACTERIZATION TECHNIQUES

This chapter briefly overviews the synthesis methodology, the characterization techniques used for the thesis, and basic instrumentation principles. The synthetic methodology for alkali metal sulfides (M_2S, M=Li or Na) and lithium silicides (Li_xSi) is depicted in Section 2.1. The subsequent section (Section 2.2) reviews the characterization techniques for understanding reaction processes and analyzing the synthesized nanomaterials. Most of the techniques depicted in this section are used to determine the product phase purity, crystallinity and morphology. Battery assembling and electrochemical analysis for the synthesized M_2S and Li_xSi are discussed in Section 2.3.

2.1 Materials Synthesis Methodology

The existing industrial M_2S synthesis is mainly based on carbothermal reduction processes and phase pure M_2S nanocrystals are commercially unavailable, as summarized in Chapter 1. Therefore, our new synthesis strategy to produce M_2S nanocrystals is of great significance for the development of next generation of rechargeable batteries. Likewise, lithium silicides are promising alternatives for developing silicon anodes and have not been well studied.\(^1\),\(^2\) Section 2.1.1 and Section 2.1.2 below will elaborate on the synthetic processes of M_2S and Li_xSi, respectively.

2.1.1 M_2S Synthesis

To synthesize M_2S nanoparticles, hydrogen sulfide (H_2S) was used to react with the respective metal (M) in the form of metalorganic complex (R-M) dissolved in an organic solution.\(^3\),\(^4\) Alkali metal naphthalenides in dimethoxyethane (DME) or alkali metal alkoxides in different solvents are used as the R-M solutions. They are first prepared in an argon (Ar) filled glove box. Typically, the molar ratio of the alkali metal to the organic reagent is set to 8:1 and the solution volume is 40 mL. Then the solution is placed in a Parr reactor to react with a premixed gas consisting of 10 atomic percent (at.%) of H_2S and 90 at.% of Ar at a total flowrate of 40 standard cubic centimeter per minute (sccm). The continuous gas flow from the gas tank to the reactor is assured by using a pump connecting to the outlet of the reactor. At the same time the gaseous effluent is sampled and analyzed using an online quadrupole mass spectrometry (QMS) connecting to the pump. Initially, the H_2S/Ar mixture flows through a bypass line for QMS analysis to measure the baseline reading, that is, the intensity of H_2S and Ar flowing out of the gas tank at the rate of 40 sccm. Then the bypass is closed and the flow is diverted through the R-M solution in the reactor at ambient temperature and normal pressure. When the molar ratio between alkali metal in the initial solution and totally supplied H_2S reaches 2.0, the gas flow is stopped simultaneously.
Subsequently, the Parr reactor is transferred into the Ar-filled glovebox and centrifugation is employed to separate the solid product out of the reaction solution. The collected solid powders are dried for analysis and electrode applications. The liquid phase is kept in the glovebox for further analysis to understand the reaction mechanisms.

2.1.2 Li$_x$Si Synthesis

Three types of lithium silicides (Li$_x$Si, $x = 4.4$, 3.75, and 2.33) are synthesized using the high-energy ball milling method, which is widely used for mechanical and mechanochemical synthesis. Briefly, in the Ar-filled glove box, appropriate amounts of Li grains, Si powders and anhydrous hexane (used as lubricant during the milling process) are loaded in a stainless-steel ball milling jar with two ½ inch balls inside. Then the well-sealed jar is taken out of the glovebox and mounted to a high-energy ball milling mixer. The milling durations are 300 min for Li$_{4.4}$Si and Li$_{2.33}$Si, and 100 min for Li$_{3.75}$Si. Last, Li$_x$Si products are collected and stored in the Ar-filled glovebox after evaporating the hexane for characterizations and electrochemical performance tests. It is easy to purify the final product due to the low boiling point of hexane.

2.2 Characterization Techniques

To study the reaction process for the synthesis of M$_2$S nanocrystals, QMS is connected to the reaction system to sample and analyse the gaseous effluent. By comparing the intensity of H$_2$S before and after the reaction, we can conclude if the reaction between H$_2$S and R-M is instant and complete. For the produced M$_2$S and Li$_x$Si powders, different characterizations are used to test the purity, crystallinity, and morphology, such as X-ray diffraction (XRD), scanning electron microscopes (SEM), and energy dispersive X-ray spectroscopy (EDX or EDS). In the following sections, the discussion focuses on the general principles and functions of these techniques.

2.2.1 Quadrupole Mass Spectrometry

QMS, one type of mass spectrometry, usually includes an electron ionizer (hot filament), a quadrupole mass filter, and a detector, shown as Figure 2.1 (page 19). As indicated by the name, the quadrupole mass filter consists of four cylindrical rods, parallel to each other, which are electrically connected. A positive voltage ($U + V\cos(\omega t)$), consisting of a direct ($U$) and an alternating ($V\cos(\omega t)$) part, is applied between two opposite rods; and a negative voltage of $-U - V\cos(\omega t)$ is applied on the other two rods to affect the movement of the ions traveling through four rods. In the QMS system, the gas is first ionized by a hot filament. Then the generated ions are separated in the quadrupole detector based on their mass-to-charge ratio ($m/z$) and the voltage applied on the rods. Voltages can be tuned in two ways: changing the angular frequency of $\omega$ and keeping $U$ and $V$ constant, or tuning $U$ and $V$ with a fixed $U/V$ ratio and keeping a constant $\omega$. Only ions with a specific $m/z$ ratio will reach the detector for the given
direct and alternating voltages, while others will collide with the rods without being detected. Therefore, a QMS spectrum, for ions with a specific m/z value or with a range of m/z values, can be obtained by varying the voltages. QMS can realize analyzing a single ion for a preset time period, as well as scanning for a range of m/z values.

Figure 2.1 Schematic of a quadrupole mass filter.

The QMS instrument we used for our M$_2$S synthesis is Stanford Research Systems RGA (residual gas analyzer) 300, containing an ionizer (hot filament), a quadrupole mass filter and a detector. The instrument has the capability of online monitoring, that is continuously sampling gaseous effluent, coupled with a pump. Hence, data can be acquired continuously, different from the batch sampling which is usually used in gas chromatography. Complete spectra can be recorded very fast, and real time intensity for selected species of interest can be measured as well.

2.2.2 X-ray Diffraction

XRD is used in this thesis to analyze the produced M$_2$S and Li$_x$Si nanoparticles. By comparing the standard patterns of M$_2$S or Li$_x$Si in the aspects of peak positions and peak intensity ratios, we can make conclusions about the phase purity, bulk crystal structure, and average crystal size based on the Debye-Scherrer equation.

XRD is based on the interaction between X-rays and the specimens, i.e., diffraction of X rays from lattice planes in crystals (shown as Figure 2.2 on page 20). An XRD instrument consists of three components: X-ray source, sample holder, and detector. In XRD instruments, X-rays are produced when electrons from a heated filament strike a metal target, which is typically a copper target that provides X-
rays with a wavelength of 0.154 nm, or a cobalt target that provides x-rays with a wavelength of 0.179 nm. In this thesis, the copper target is used in the Philips X’Pert XRD instrument.

The general principle of XRD is based on Bragg’s law of \( n\lambda = 2d\sin\theta \), where \( d \) is the spacing between diffracting planes of the crystal, \( \theta \) is the incident angle, \( n \) is the diffraction order with the value of any integer, and \( \lambda \) is the wavelength of the X-ray beam. When X-rays are bombarding the crystal sample, X-rays will be deflected by twice the incident angle (2\( \theta \)) to reach the detector. When the difference in the path lengths (2\( d\sin\theta \)) between two waves is equal to an integer (\( n \)) multiple of the X-ray wavelength (\( \lambda \)), a constructive interference occurs between these two waves, producing peaks at the corresponding position of \( 2\theta \), shown as Figure 2.2.\(^{11}\) Two of the three XRD components (X-ray source, sample holder, and detector) must move to allow for each angle to be analyzed. In the Philips X’Pert XRD the sample holder is fixed, while the detector and X-ray source are the moving components.

![Figure 2.2 Schematic of the Bragg’s diffraction.](image)

XRD essential for identifying the crystal structure, estimating the average crystal size of the nano crystalline samples, and investigating the effect of lattice strain. Larger broadness of XRD peaks indicates smaller crystal size. The Scherrer equation (\( D = \frac{K\lambda}{\beta\cos\theta} \), where \( D \) is the crystal size; \( K \) is the dimensionless shape factor; \( \lambda \) is the X-ray wavelength; \( \beta \) is the full width at half maximum intensity for the XRD peak; and \( \theta \) is the Bragg’s angle) can be used to predict the crystal size if crystals are smaller than 100 nm. Effect of lattice strain can also be studied based on the diffraction peak position and width. Uniform strain on the crystal structure will cause peak shift,\(^2,12\) while non-uniform strain results in peak broadness.\(^{13} \)
Limitations of XRD are that it is not applicable to amorphous phases and that sample amounts need to be relatively large due to the relatively low sensitivity.\textsuperscript{14, 15} In addition, the average crystal size estimation using the Scherrer equation is not accurate for large crystal size. Therefore, complementary characterizations are usually needed to corroborate the size results obtained from XRD.

### 2.2.3 Scanning Electron Microscopy

SEM uses a focused beam of high-energy electrons to interact with the sample, generating a variety of signals of secondary electrons, backscattered electrons, and characteristic X-rays that contain information about the sample's surface topography and composition.\textsuperscript{16}

Electron beams are critical in the SEM instrument, governing the image resolution. Field emission scanning electron microscope (FESEM) is used in this thesis. The difference between standard SEM and FESEM is the sources to generate electron beams.\textsuperscript{17} In the standard SEM, electron beams with the diameter of \(~10\text{-}30\ \mu\text{m}\) are mostly generated by heating a tungsten (W) or lanthanum hexaboride (LaB\textsubscript{6}) filament. However, in FESEM, the intensive and monochromatic electronic beam with the diameter of \(~5\ \text{nm}\) is liberated from a pointed single crystal W filament applied with high electrostatic field emission which requires an extreme vacuum (\(\leq 10^{-8}\ \text{Torr}\)). The resolution of FESEM images is markedly improved because the electron beam produced by the field emission source is about 1000 times smaller than that in a standard microscope.\textsuperscript{17}

Secondary electrons are emitted by atoms near the surface of the sample when their electrons become excited and have enough energy to escape the sample surface. Secondary electron imaging is the common detection mode in SEM imaging. Secondary electrons have relatively low energy and only those near the surface of the sample are able to escape out of the sample and be detected. The angle and intensity of the detected secondary electrons from each location of the sample are related to the surface topography, providing morphology images of the sample.\textsuperscript{18}

Some electrons from the incident beam are backscattered by sample atoms and re-emerge from the sample surface, called backscattered electrons. The depth of backscattered electrons is larger than that of secondary electrons, resulting a poorer resolution of the surface topography.\textsuperscript{19} However, the intensity of backscattered electrons is strongly related to the atomic numbers of the nuclei in the specimen. For example, heavier elements in the samples backscatter more efficiently and show brighter backscattered electron image than lighter elements. Therefore, they are usually used to analyze the distribution of different elements in the sample, such as EDS.\textsuperscript{19}

EDS is a powerful technique used in conjunction with SEM for analyzing the elemental composition of a specimen by detecting the characteristic X-ray information. When the electron beam interacts with the sample, along with secondary and backscattered electrons, electrons from inner shell of
the sample elements are excited and leave behind holes. Then the generated hole in the excited atom is filled with an electron from an outer shell, relaxing to the ground state. At the same time, the X-ray is emitted to release the excess energy. The energy of the emitted X-rays is specific to the atom type (energy difference between two electron shells). A detector is used to convert the X-ray energy signal into voltage signal which is then sent to a computer for data display and analysis. As a result, an EDS spectrum with multiple peaks indicates multiple elements in the sample. Furthermore, quantitative data regarding the elemental distribution, mass and molar ratio in the sample can be obtained based on the intensity of X-rays reaching the detector for each element. Limitations for EDS include the low precision of the quantitative analysis and the inability to detect light elements such as hydrogen and lithium.

2.3 Battery Assembling and Performance Assessments

A significant part of the thesis is to study the electrochemical performance using the synthesized materials of $\text{M}_2\text{S}$ nanocrystals or $\text{Li}_x\text{Si}$ nanoparticles in lithium ion batteries (LIBs). One LIB, usually consists of two electrodes (one anode and one cathode allowing lithium ions to move in and out of their structures), a separator (usually a porous membrane, placed between anode and cathode, permeable to ionic flow but preventing electric contact of two electrodes) and the electrolyte (transporting the lithium ions). In practice, in the cathode and anode, active electrode materials are integrated with other essential components, such as binders and conductive additives. To focus on the synthesized electrode materials (working electrode), we assembled lithium half batteries (or half cells) by using a piece of lithium foil as the counter electrode and reference electrode.

All lithium-ion batteries work generally in the same way. During the charging or energy-storing step, the lithium ions ($\text{Li}^+$) are extracted out of the cathode, moving through the separator and electrolyte, and inserted to the anode. During the discharging or energy-releasing process, lithium ions move back to the cathode through the separator and electrolyte. In both processes, electrons and Li-ions flow in the same directions to meet at the same electrode by crossing the external circuit and the internal circuit, respectively.

The primary parameters for the battery performance evaluation include cell voltage (the difference in the redox potentials between the anode and cathode), specific capacity (the amount of charge supplied per unit of mass), cycling stability or cyclability (the ability of an electrode can maintain the original capacity during charging/discharging cycles), capacity retention (ratio of the charging or discharging capacity for subsequent cycles versus the initial value), Coulombic efficiency (the ratio of the charge output to the charge input of the same cycle).

Specific capacity for the electrode material is a fundamental characteristic of the material, and depends upon its redox chemistry. For a given active material, the theoretical value of the specific capacity
(SC) can be calculated according to: \[ SC \text{ (mAh/g)} = xF \text{ (sA/mol)} \times 1000 \text{ (mA/A)} / (3600 \text{ (s/h)} \times MW \text{ (g/mol)}) \], where \( x \) is number of electrons or lithium ions transferred in the reaction, \( F \) is Faraday constant, and \( MW \) is molecular weight of the material. For example, for the graphite anode whose electrochemical reaction is \( 1/6 \text{ Li}^+ + 1/6 \text{ e}^- + C \rightarrow 1/6 \text{ LiC}_6 \), the theoretical SC is: \[ SC = xF \text{ (sA/mol)} * 100 \text{ (mA/A)} / (3600 \text{ (s/h)} \times MW \text{ (g/mol)}) = 1/6 \times 96485 \text{ (sA/mol)} \times 1000 \text{ (mA/A)} / (3600 \text{ (s/h)} \times 12 \text{ (g/mol)}) = 372 \text{ mAh/g}. \]

Cycling stability (the specific capacity versus cycling numbers) measures the reversibility of the charge input and output processes and can be obtained by repeating the discharging and charging processes at a certain current (named as galvanostatic test) between a designated potential/voltage window. Ideally, the capacity value is steady without decaying throughout cycling. However, due to chemical changes of the electrodes caused by side reactions on the interface between the electrolyte and electrode during the cycling process, capacity always decays. The discharging current for the cycling stability test is often expressed in relation to the theoretical capacity, which is known as the C-rate. For example, with a theoretical capacity of 100 mAh, the current at rate of C/n (n is any positive number) is 100/n mA, to discharge the battery completely in n hours.

Voltage profile (voltage (V) versus charging or discharging capacity (Q)) and differential capacity analysis (dQ/dV) versus voltage during the charging or discharging are used to analyze the redox reactions over a cycle-life test. Compared with the voltage profile, the advantage of dQ/dV analysis is that the voltage plateaus in the voltage profile appear as sharp or pronounced peaks in dQ/dV. Hence, dQ/dV is more sensitive to measure the voltages for the specific electrochemical reactions.

Cyclic voltammetry (CV) is an important and widely used electroanalytical technique for lithium ion batteries. It can be implemented on a potentiostat by scanning the potential across a specified potential range at a constant rate (linearly related to time for each half cycle) and measuring the resultant current. CV is powerful to study oxidation and reduction behaviors (such as the reversibility, phase transition, and activation potential) of the electrode materials. Figure 2.3 (page 24) is a typical CV plot showing the measurable parameters including the anodic reaction peak position of \( E_{pa} \) and the current intensity of \( i_{pa} \); the cathodic reaction peak position of \( E_{pc} \) and the current intensity of \( i_{pc} \). When the potential is scanned past the potential of \( E_{pa} \) from the lower value to the higher value, the reduced form is converted to the oxidized form, which is also named as the anodic reaction. When the direction of the potential sweep is reversed, the reduction reaction or cathodic reaction occurs.

For a simple reversible redox, the values of \( i_{pa} \) and \( i_{pc} \) should be identical, that is, \( i_{pa}/i_{pc}=1 \). Another parameter to evaluate the reversibility of the redox couple is the separation between the peak potentials \( E_{pa}-E_{pc} \), which should be equal to 0.059/n with the unit of V at room temperature, where \( n \) is the number of electrons transferred in the electrochemical reaction.
In our battery analysis using two-electrode cells, the potential and current of the working electrode are measured versus the Li⁺/Li reference electrode which also functions as the counter electrode. CV is a standard technique to understand the electrochemical reactions during charging and discharging processes. The small peak position difference between the CV profiles and the dQ/dV plots can be explained by the different reaction kinetics and polarization effects in the CV measurement and the galvanostatic cycling.

Figure 2.3 A typical CV figure showing the measurable parameters.

Another important electrochemical characterization for rechargeable batteries is electrochemical impedance spectroscopy (EIS), which can reveal useful information about dynamics of the electrochemical processes on electrode interfaces. EIS is usually measured by applying a small alternating potential (~10 mV) over a wide range of frequencies (0.01 Hz – 1 MHz) to an electrochemical cell and testing the current flow which encounters a number of impedance interactions inside materials and at interfaces (such as the electrode/electrolyte interface) between two electrodes. The alternating potential can be expressed as: \( E = E_0 \sin(\omega t) \), where \( E_0 \) is the amplitude of the signal, and \( \omega \) is the angular frequency. The responding current of the system is expressed as: \( I = I_0 \sin(\omega t + \theta) \). According to the Ohm's Law, the impedance can be calculated according to Equation 2.1 or Equation 2.2. Therefore, there are both real and imaginary parts in the impedance. A Nyquist plot (Figure 2.4 on page 25) with the real part as X axis and imaginary part as Y axis is usually used to present the EIS results. Each datum point on the Nyquist plot is the impedance at one specific frequency.
\[
Z = \frac{E}{I} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \theta)}
\]

\[
Z = \frac{E}{I} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \theta)} = Z_0 \exp(j\theta) = Z_0 (\cos \theta + j \sin \theta)
\]

In rechargeable batteries, an electrode impedance spectrum usually includes one semicircle and one straight line (Figure 2.4). EIS data are analyzed by fitting to an equivalent electrical circuit model integrating different electrical elements such as resistors and capacitors in serial or parallel models representing different interfaces in the battery. Randles equivalent circuit\(^\text{28}\) is one of the most common cell models and the starting point for building more complex models. In Figure 2.4, the x-axis intercept represents the resistance from the electrode and the electrolyte solution \((R_\Omega)\). The semicircle can be fitted with the charge transfer resistance \((R_{\text{ct}})\) in parallel with the double-layer capacitance \((C_d)\). The larger diameter of the semicircle, the higher the charge transfer resistance. The straight line at low frequency is attributed to the Warburg impedance \((W)\), a measurement of the mass diffusion resistance in the electrode. The semicircle and the linear part are important to analyze the redox reaction kinetics. In rechargeable batteries, the impedance usually changes with increasing cycles, which helps to know the influence of the electrode impedance on the cycling performance.

![Figure 2.4 Schematic of a typical Nyquist plot with the Randles equivalent circuit on the top.](image)

2.4 References


CHAPTER 3
THERMODYNAMICALLY FAVORABLE CONVERSION OF HYDROGEN SULFIDE INTO VALUABLE PRODUCTS THROUGH REACTION WITH SODIUM NAPHTHALENIDE

Xuemian Li,† Rachel M. Morrish,§ Yuan Yang,§ Colin A. Wolden,‡ and Yongan Yang*†

3.1 Abstract
Hydrogen sulfide (H$_2$S) is an extremely hazardous chemical waste that is generated at large scale in many industries; its abatement has long been an energy-extensive and cost-ineffective liability due to the thermodynamic limitations of the selected approaches and low value of the final products, sulfur and water. Here we introduce an attractive method for H$_2$S abatement that yields value-added products via a thermodynamically favorable process. Specifically, sodium naphthalenide (Na-NAP) is used to capture H$_2$S to produce anhydrous Na$_2$S nanocrystals and 1,4-dihydronaphthalene, which are important materials for batteries and liquid fuels, respectively. This multipurpose process is driven by the acid/base neutralization reaction between hydrogen cations from H$_2$S and radical anions from naphthalenide. It is spontaneous and irreversible at ambient temperature and pressure, proceeding to completion very rapidly.

3.2 Introduction
Hydrogen sulfide (H$_2$S) is a major chemical waste produced predominantly through desulfurization of natural gas and petroleum reserves.¹ It is extremely hazardous to human health,² corrosive to equipment,³ and poisonous to catalysts.⁴ Thus, cleaning H$_2$S is an inevitable liability. For several decades, the most prevailing and successful technique for H$_2$S abatement in the oil and natural gas industries is the Claus process, which utilizes air to partially oxidize H$_2$S to S and H$_2$O in two steps with the overall reaction expressed by Equation 3.1.⁵ ⁶

$$\text{H}_2\text{S} + 1/2\text{O}_2 \xrightarrow{\Delta G_{\text{in}}^{\circ}=204\text{kJmol}^{-1}} \text{S} + \text{H}_2\text{O}$$

---

† Primary author
§ Coauthor
* Corresponding author
¹ Department of Chemistry, Colorado School of Mines
² Department of Chemical and Biological Engineering, Colorado School of Mines
While this reaction is thermodynamically favorable, its practical operation remains energy intensive and cost ineffective, because 1) it needs high temperature (ca.1300 K); 2) the tail gas still contains a few percent of unreacted H$_2$S and SO$_2$ and needs further treatments; 3) the S produced exceeds demand and is sold at a loss; and 4) the byproduct H$_2$O is undesirable, particularly for oil refinery industries where the hydrogen in H$_2$S originates from expensive H$_2$ gas. Other approaches that employ scavengers (such as organoamines, porous materials, metal oxides/salts, biological oxidation, or caustic soda) produce no valuable products and must be periodically regenerated, creating additional waste streams. Combustion is not a practical option as it generates SO$_2$, itself a highly regulated chemical as the precursor to acid rain.

Perhaps the most aesthetically pleasing approach for H$_2$S abatement would be decomposition into its elemental constituents (Equation 3.2). Numerous techniques have been pursued to conduct Reaction 3.2, such as thermal decomposition, thermochemical conversion, plasmochemical decomposition, photochemical decomposition, electrochemical decomposition, and photoelectrochemical decomposition. However, they all suffer from the common challenge that Reaction 3.2 is thermodynamically unfavorable and significantly endothermic, which limits the commercial viability. In summary, methods that can convert H$_2$S to value-added products via thermodynamically favorable pathways are highly desirable.

\[
\text{H}_2\text{S} \xrightarrow[\Delta G_{m}^{\circ} = 334 \text{kJ mol}^{-1}]{\text{H}_2\text{S}} \xrightarrow[\Delta G_{m}^{\circ} = -300 \text{kJ mol}^{-1}]{\text{H}_2\text{S}} \text{H}_2 + \frac{1}{8} \text{S}_8
\] (3.2)

Therefore, we aim to address H$_2$S remediation through reaction with alkali metals as described by Equation 3.3, where M=Li, Na, K. The very negative Gibbs free energy ($\Delta G_{m}^{\circ}$) implies that this reaction is thermodynamically favorable and expected to be spontaneous and irreversible. A significant benefit of this chemistry is the accompanying synthesis of valuable M$_2$S, an attractive cathode material for alkali metal/sulfur (M–S) batteries. Existing technologies for the production of anhydrous M$_2$S are complex, energy inefficient, and not environmentally benign. As M$_2$S is many times much more valuable than M, the proposed technique has the potential to be practically attractive even without H$_2$ generation. Thus, this new synthetic approach deserves a systematic exploration.
Herein we introduce an efficient abatement of \( \text{H}_2\text{S} \) through scrubbing an \( \text{H}_2\text{S}/\text{Ar} \) gas stream with a solution of sodium-naphthalene (Na-NAP, \( \text{NaC}_{10}\text{H}_{8} \)). The reaction between Na-NAP and \( \text{H}_2\text{S} \) proceeds spontaneously to completion at ambient temperature and pressure, reducing \( \text{H}_2\text{S} \) to below detection limit. Highly-pure, crystalline \( \text{Na}_2\text{S} \) nanoparticles are produced as well as a small amount of \( \text{H}_2 \) in accordance with Reaction 3.3, but the majority of the hydrogen released from \( \text{H}_2\text{S} \) hydrogenates naphthalene to form 1,4-dihydronaphthalene, a valuable byproduct commonly known as 1,4-dialin that is used as an organic solvent and jet fuel.\(^{25, 26}\)

### 3.3 Results and Discussion

The proof-of-concept experiment was completed as shown in Figure 3.5 (page 40). A dimethoxyethane (DME) solution containing 0.04 M of Na-NAP in a Parr reactor was supplied with a premixed gas consisting of 10 atom % \( \text{H}_2\text{S} \)/90 atom % \( \text{Ar} \). The effluent was sampled in line using a differentially pumped quadrupole mass spectrometer (QMS). When the molar ratio between Na in the initial solution and \( \text{H}_2\text{S} \) totally supplied reached 2.0, the inlet and outlet were closed simultaneously.

Figure 3.1A (page 31) plots the relative concentrations of \( \text{H}_2\text{S} \) (black) and \( \text{H}_2 \) (red) recorded by the QMS. Upon diversion of the \( \text{H}_2\text{S} \) stream from the bypass into the reactor (marked by the arrow), the \( \text{H}_2\text{S} \) signal immediately began to fall and eventually dropped below the detection limit of the instrument, indicating that at least >99.9 % of \( \text{H}_2\text{S} \) supplied was consumed. The characteristic timescale of \( \text{H}_2\text{S} \) depletion herein reflects the gas dynamics of the sampling apparatus, identical to the response observed by closing a valve. The mass spectrum obtained during the bypass mode (Figure 3.1B, black) clearly shows the expected fragments of \( \text{H}_2\text{S} \) across mass/charge (\( m/z \)) ratios of 32–34. In contrast, the spectrum recorded from the effluent (Figure 3.1B, red) presents no signals from \( \text{H}_2\text{S} \) but the expected Ar signal. Additionally, the gasses from the head space in the reactor were flushed through a 0.1 M \( \text{AgNO}_3 \) solution; the observation of no precipitate (\( \text{Ag}_2\text{S} \)) indicated that the residual \( \text{H}_2\text{S} \) at the end of the reaction was below \( 2.2 \times 10^{-40} \) ppb.\(^{27}\) This result was consistent with the equilibrium concentration of \( \text{H}_2\text{S} \) residue predicted by the extreme negative \( \Delta G_m^0 \) value. Thus, we concluded that the demonstrated \( \text{H}_2\text{S} \) removal with Na-NAP was spontaneous, complete, and nearly instantaneous.

Comparisons to calibrated mixtures revealed that the maximum amount of \( \text{H}_2 \) generated (Figure 3.1A) did not exceed 1.5% of the amount expected, if \( \text{H}_2\text{S} \) was completely converted to \( \text{H}_2 \) as indicated by Equation 3.4.\(^7\) This suggested that the hydrogen was captured in the solution as expected (vide infra). The X-ray diffraction (XRD) pattern of the solid product shown in Figure 3.1C (blue), matches that of the \( \text{Na}_2\text{S} \) standard (black), indicating the production of anhydrous, phase-pure, crystalline \( \text{Na}_2\text{S} \). The scanning electron microscope (SEM) image (inset) shows that
Na$_2$S existed as nanoparticles less than 100 nm in diameter.

$$2\text{NaC}_{10}\text{H}_8 + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{Na}_2\text{S} + 2\text{C}_{10}\text{H}_8$$  \hspace{1cm} (3.4)

![Figure 3.1](image)

Figure 3.1 Demonstration of the proposed concept of removing H$_2$S using Na-NAP. A) Real-time QMS measurements of the relative changes in H$_2$S and H$_2$ upon introduction of H$_2$S to Na-NAP. B) Mass spectra showing that the 10% of H$_2$S in Ar (black) is completely removed after treatment (red). C) XRD pattern (blue) and SEM image (inset) of the solid product and XRD stick pattern (black) of the Na$_2$S standard.

We anticipated that hydrogen was retained in the solution in the form of hydrogenated NAP (i.e., 1,4-dihydronaphthalene C$_{10}$H$_{10}$) as expressed in Equation 3.5. To confirm this, the liquid phase after reaction was characterized by FTIR spectroscopy and $^1$H-NMR spectroscopy (Figure 3.2 on page 32). The crude solution was concentrated through rotary vaporization, by taking
advantage of the low boiling point (85 °C) of the DME solvent, the tendency of NAP to sublime, and the high boiling points (> 200 °C) of NAP derivatives. The FTIR spectrum was taken on the solid residue left after a droplet of the solution applied to the attenuated total reflection (ATR) crystal had dried. The spectrum (Figure 3.2A) has characteristic features of 1,4-dihydronaphthalene (the dihydrogenated NAP). The 1H-NMR spectrum (Figure 3.2B) was taken by dispersing liquid product in C₆D₆. In addition to the expected DME, benzene, and NAP, three weak peaks at 6.91 - 5.66 pm can be assigned to the hydrogen atoms at positions (a) and (b) of 1,4-dihydronaphthalene. The signal from the hydrogen atoms at position (c), expected to be at 3.3 - 2.9 ppm, are believed to be buried within the intense DME signal.

\[
2\text{NaC}_{10}\text{H}_8 + \text{H}_2\text{S} \rightarrow \text{Na}_2\text{S} + \text{C}_{10}\text{H}_{10} + \text{C}_{10}\text{H}_8 \quad (3.5)
\]

Figure 3.2 Characterization of the organic compounds in the liquid phase. A) FTIR spectrum of the solid residue after removal of NAP and DME. B) 1H NMR spectrum of the liquid phase directly from the reaction system.

To collect more convincing evidence for the production of 1,4-dihydronaphthalene, the liquid phase was further analyzed by gas chromatography/mass spectroscopy (GC-MS) using DME as the solvent. The chromatogram in Figure 3.3A (page 33) shows two peaks. The mass spectrum for peak 1 is well consistent with that of 1,4-dihydronaphthalene in the literature. The mass spectrum for peak 2 is well consistent with that of NAP. Thus, the characterization results discussed above all together confirm that the Na-NAP strategy of removing H₂S follows the overall transformation described by Equation 3.5 with 1,4-dihydronaphthalene being the principle NAP derivative.
The elementary reactions for this process are shown in Scheme 3.1 (page 34) with details described in the Supporting Information (SI). This mechanism, the basis for us to devise the multipurpose process herein, was derived from two sets of literature results. First, a similar mechanism has been determined for producing 1,4-dihydronaphthalene from alcoholysis of NaNAP in ammonia (or alkylamines such as ethylenediamine).\textsuperscript{30} Second, hydrolysis of NaNAP/DME produces 1,4-dihydronaphthalene and NaOH, without evolution of H\textsubscript{2}.\textsuperscript{31} H\textsubscript{2}S, as alcohols and water, can also provide dissociated protons.\textsuperscript{30-32} To the best of our knowledge, there have not been studies of hydrogenating NAP using a chemical waste like H\textsubscript{2}S. The minor amount of H\textsubscript{2} production in competition with the production of the NAP derivative is ascribed to the reversed electron transfer from naphthalenide radicals to H\textsuperscript{+} ions, producing H radicals that dimerize to H\textsubscript{2}.

Figure 3.3 GC–MS analysis of the liquid phase of the reaction system: (A) the chromatogram; (B) the MS spectrum for peak 1 in (A); and (C) the MS spectrum for peak 2 in (A).
Scheme 3.1 The proposed reaction mechanism of removing H$_2$S with Na-NAP to produce 1,4-dihydronaphthalene through a radical hydrogenation reaction. Intermediates: An NAP molecule (1) receives an electron from Na; an NAP$^-$ radical (2), a hydrogenated NAP$^-$ radical (3), a hydrogenated NAP$^-$ anion (4), and a 1,4-dihydronaphthalene molecule (5).

To better understand the mechanism of the formation of Na$_2$S, we conducted three more reactions in which the Na-NAP/H$_2$S molar ratio was controlled at 1.0, 1.1, and 3.4. Figure 3.4 (page 35) shows the XRD data of the solid products in these three cases. In the case of Na-NAP/H$_2$S=1.0 (Figure 3.4A), the product is pure, anhydrous, crystalline NaHS. In the case of Na-NAP/H$_2$S=1.1 (Figure 3.4B), a tiny amount of Na$_2$S is also detectable (as marked by the arrow) in addition to the predominate NaHS. In the case of Na-NAP/H$_2$S=3.4 (Figure 3.4C), the product is pure, anhydrous, crystalline Na$_2$S.

From the XRD results in Figure 3.1C (page 31) and Figure 3.4 we surmise that under conditions where the Na-NAP/H$_2$S ratio is $\geq$ 2, the Na$_2$S is the only solid product, and this appears to occur directly and instantly, supporting the reaction mechanism in Scheme 3.1. When additional H$_2$S is added to the system beyond the stoichiometric ratio, NaHS is formed according to Equation 3.6, as reported in the literature for high-temperature reactions.\footnote{33}

\begin{equation}
\text{Na}_2\text{S} + \text{H}_2\text{S} \rightarrow 2\text{NaHS}
\end{equation}

All reactions appear to be very fast since the product distribution appears to reflect the stoichiometric ratio of the two reactants, as otherwise it would be difficult to observe the tiny amount of Na$_2$S in the case of Na-NAP/H$_2$S = 1.1. While Na$_2$S is the preferred product for battery applications, the second reaction doubles the capacity of the Na-NAP solution for H$_2$S abatement and provides the flexibility to tune the reaction products. For instance, NaHS is a valuable chemical for many industries, such as paper and pulp and leather manufacturing and mining.\footnote{34, 35}

All reactions appear to be very fast since the product distribution appears to reflect the stoichiometric ratio of the two reactants, as otherwise it would be difficult to observe the tiny amount of Na$_2$S in the case of Na-NAP/H$_2$S = 1.1. While Na$_2$S is the preferred product for battery applications, the second reaction doubles the capacity of the Na-NAP solution for H$_2$S abatement and provides the flexibility to tune the reaction products. For instance, NaHS is a valuable chemical for many industries, such as paper and pulp and leather manufacturing and mining.\footnote{34, 35}
Figure 3.4 XRD data of the solid products in three reactions using different Na-NAP/H$_2$S molar ratios: 1.0 (A), 1.1 (B), and 3.4 (C). The standard XRD patterns (sticks) of the predominate chemicals are shown as references.

3.4 Conclusion

In conclusion, we have reported an innovative process for efficiently removing H$_2$S and producing value-added products through a thermodynamically favorable reaction. The concept is demonstrated by using sodium naphthalenide (Na-NAP) to convert H$_2$S into nanocrystalline Na$_2$S (a battery material) and 1,4-dihydronaphthalene (a liquid fuel). Moreover, this irreversible reaction spontaneously proceeds to completion at ambient temperature and pressure. This is an attractive technique for M$_2$S synthesis compared with the existing approaches, which either need H$_2$S-derived S and M as precursors or require extensive procedures to remove impurities when cheap precursors (such as Na$_2$SO$_4$ and carbon) are used. The introduction of this technique would be expected to complement but not replace the Claus process. In addition, it is expected that reactive species commonly found in industrial H$_2$S waste streams (such as H$_2$O, O$_2$, and CO$_2$) should be removed before employing this technique. While this pretreatment adds extra costs and alkali
metals are expensive, the operation costs could be offset by high-value M₂S and 1,4-dihydronaphthalene. Work is underway to assess battery performance of Na₂S, generalize this technique to Li and K, explore other reducing agents for obtaining more H₂ gas, and study the sensitivity of the process to impurities.

3.5 Experimental Section

3.5.1 Materials

Sodium metal (Na, ACS reagent grade, stick dry), naphthalene (NAP, C₁₀H₈, 99 %), 1,2-dimethoxyethane (DME, anhydrous, 99.5 %), and hexane (ACS grade) were purchased from Aldrich. [D₆]-Benzene (d-99.5 %) was purchased from Cambridge Isotope Lab. Silver nitrate (AgNO₃, 99.9+ %) was purchased from Alfa Aesar. All chemicals were used as received.

3.5.2 Methods

A typical reaction was run as follows. Appropriate amounts of NAP and Na at the molar ratio of NAP/Na=1.3 were sequentially added to DME in an argon-filled glove box to make a DME solution containing 0.04 M of sodium naphthalenide (Na-NAP). A dark green color is immediately observed upon addition of the Na, and a homogenous solution was obtained after two hours of stirring (Figure 3.5). Then, the Na-NAP solution (50 mL) was placed in a Parr reactor (model 4793). After that, the reactor was connected to the gas line containing 10 atom % H₂S/90 atom % Ar. A schematic diagram and a photograph of the apparatus are shown in Figure 3.5B and C, respectively. Initially, the H₂S/Ar mixture was passed through a bypass line at a flow rate of 40 sccm to establish a baseline reading. Then, the bypass was closed and the H₂S/Ar flow was diverted through the Na-NAP solution, which was kept at ambient temperature and pressure. The effluent was evacuated using vacuum pumps and sampled in line using a differentially pumped quadrupole mass spectrometer (QMS). The overall molar ratio of Na-NAP to H₂S supplied was controlled by controlling the duration of the H₂S flow.

After the reaction, the reactor was connected to an Ar line to flush the gas phase out of the reactor into a 0.1 M AgNO₃ solution (1 mL). The purpose was to observe if any precipitate would be generated, indicating the formation of Ag₂S and in turn the existence of unreacted H₂S in the reactor. Based on the extremely low solubility of Ag₂S \( (K_{sp}=10^{-50.1}) \), the detection limit of H₂S in the reactor was as low as 2.2 \( \times 10^{-40} \) ppb.

Then, the reactor was transferred into an Ar-filled glove box. The reaction solution was centrifuged to separate the solid phase and the liquid phase. The solid phase was washed with DME several times and dried for further characterization. The liquid phase was removed from the glove box and concentrate via rotary evaporation to 1/5 of the original volume. After that, the solution was stored in the glove box for further characterization.
3.5.3 Sample Analysis and Characterization

The in line QMS measurements were obtained using a Stanford Research Systems RGA300 by sampling the reactor effluent through a differentially pumped orifice. X-ray diffraction (XRD) patterns were collected on a Philips X’Pert X-ray diffractometer using Cu Kα radiation (λ=0.15405 nm). The samples were prepared in an argon-filled glove box by pouring solid products onto glass substrates. To prevent detrimental reactions due to the inevitable air exposure during measurements, the solid was immediately covered with a drop of dried mineral oil in the glove box. The background contribution from mineral oil featured a broad peak centered at 17.2° with a width from 10 to 25° and was corrected before analysis. Fourier transform infrared (FTIR) spectroscopy was performed on a Thermo Scientific Nicolet iS50 spectrometer using the attenuated total reflection (ATR) mode for powder samples at a spectral resolution of 2 cm⁻¹. For ¹H NMR analysis (JEOL ECA-500), 0.3 mL of the concentrated liquid phase was dissolved in 0.2 mL of [D₆]-benzene and loaded in a quartz NMR tube. For the GC–MS analysis, a Varian CP-3800 GC with a 5% diphenyl-, 5% dimethyl-polysiloxane column coupled to a Varian 1200L quadrupole mass spectrometer was employed. The column was first preconditioned at 320 °C by injecting pure solvent DME. And then, the sample solution (1 μL) was analyzed using the column temperature of 250 °C. The flow rate of the He carrier gas was 1.3 mL min⁻¹.

3.6 Acknowledgements

This work is financially supported by the Startup Fund for Y.Y. from the Colorado School of Mines (CSM). C.A.W. and R.M.M. acknowledge support by the National Science Foundation through award DMR-1207294.

3.7 Keywords

hydrogen sulfide, naphthalene, radicals, sodium, sodium sulfide

3.8 References


(28) "Spectral Database for Organic Compounds SDBS". *National Institute of Advanced Industrial Science and Technology (AIST).*

(29) NIST14 and Wiley databases. 2014.


3.9 Supporting Information

3.9.1 Figure

Figure 3.5 Photograph of the Na-NAP solution (A), schematic diagram (B) and photograph (C) of the reaction apparatus used for the proof-of-concept.

3.9.2 The Reaction Mechanism

The elementary reactions mechanism for this process are shown in Scheme 3.1 (copied here). First, an electron from Na donates to NAP (1), resulting in the bond rearrangement of NAP to produce an anion radical (2, NAP$^-$). Second, a nucleophilic reaction occurs between the negatively-charged carbon in (2) and one proton (H$^+$) dissociated from H$_2$S, forming a molecular radical (3). Third, a second electron migrating from another Na-NAP binds with (3) to form an anion (4). Forth, the second proton from the previously generated HS$^-$ reacts with (4) to produce 1,4-dihydronaphthalene (5). The overall reaction can be considered as the reduction of NAP with two hydrogen atoms. Two NAP radicals (2) are needed to produce one molecule of 1,4-dihydronaphthalene (5).  

Scheme 3.1 The proposed reaction mechanism of removing H$_2$S with Na-NAP to produce 1,4-dihydronaphthalene through a radical hydrogenation reaction: An NAP molecule receiving an electron from Na (1); an NAP$^-$ radical (2); a hydrogenated NAP$^-$ radical (3); a hydrogenated NAP$^-$ anion (4); and a 1,4-dihydronaphthalene molecule (5).
CHAPTER 4
FACILE SYNTHESIS OF LITHIUM SULFIDE NANOCRYSTALS FOR USE IN ADVANCED RECHARGEABLE BATTERIES

A paper published in ACS Applied Materials & Interfaces, reproduced by permission of American Chemical Society (ACS).
DOI: 10.1021/acsami.5b09367 ACS Appl. Mater. Interfaces 2015, 7, 28444-28451
Xuemin Li,† Colin A. Wolden,* Chunmei Ban,§ and Yongan Yang*†

4.1 Abstract

This work reports a new method of synthesizing anhydrous lithium sulfide (Li2S) nanocrystals and demonstrates their potential as cathode materials for advanced rechargeable batteries. Li2S is synthesized by reacting hydrogen sulfide (H2S) with lithium naphthalenide (Li-NAP), a thermodynamically spontaneous reaction that proceeds to completion rapidly at ambient temperature and pressure. The process completely removes H2S, a major industrial waste, while cogenerating 1,4-dihydronaphthalene, itself a value-added chemical that can be used as liquid fuel. The phase purity, morphology, and homogeneity of the resulting nanopowders were confirmed by X-ray diffraction and scanning electron microscopy. The synthesized Li2S nanoparticles (100 nm) were assembled into cathodes and their performance was compared to that of cathodes fabricated using commercial Li2S micropowders (1 - 5 µm). Electrochemical analyses demonstrated that the synthesized Li2S were superior in terms of (dis)charge capacity, cycling stability, output voltage, and voltage efficiency.

† Primary author
§ Coauthor
* Corresponding author
1 Department of Chemistry, Colorado School of Mines
2 Department of Chemical and Biological Engineering, Colorado School of Mines
3 National Renewable Energy Laboratory
4.2 Keywords
lithium sulfide, lithium-sulfur batteries, synthesis, hydrogen sulfide, lithium naphthalenide

4.3 Introduction
Rechargeable batteries are ubiquitous power sources in our modern society. Their applications span from personal devices to national defense, from chemical sensors to human health, and from ground transportation to spacecrafts.1-3 Currently, the most advanced rechargeable batteries are lithium-ion batteries (LIBs, which typically employ graphite anodes and lithium cobalt oxide cathodes).4 While they are superior to conventional counterparts (such as nickel-cadmium batteries), more advanced LIBs and beyond-Li technologies with higher specific energy (energy per unit mass), higher energy density (energy per unit volume), lower cost, and safer chemistry/fabrication are imperative to meet the demand of sustainable development.4

Lithium-sulfur (Li-S) batteries are widely considered the most promising power sources in the near future for developing more advanced portable devices, electric vehicles (EVs), and stationary energy-storage facilities.5 Compared with the current generation LIBs, Li-S batteries hold two remarkable advantages:5, 6 (1) presenting higher specific energy (2600 vs. 580 Wh/kg) and energy density (2200 vs. 1800 Wh/L); and 2) using earth-abundant and cost-effective materials in the cathode (S vs Co). However, the direct use of a lithium metal anode and a sulfur cathode ensues some challenges.7-9 First, cycling can lead to the formation of harmful dendrites on the lithium metal anode, which can grow and penetrate the separator, potentially causing short-circuit, thermal runaway, and even severe fire.8, 10 Second, it is difficult to engineer the sulfur cathode to provide sufficient void space to accommodate the 80% volume expansion that accompanies lithiation, which often pulverizes the electrode and damages the electrical contact.8 An alternative approach that avoids these problems is to use lithium sulfide (Li₂S) as the cathode.11

While Li₂S and sulfur are both poor electronic and ionic conductors, which would typically preclude their use in electrochemical applications, Li₂S presents several advantages.11 First, the use of Li₂S avoids the problems associated with lithium metal anodes, and it can directly be paired with existing anode materials (graphite) as well as new lithium-free materials (such as silicon and tin) for assembling batteries.12 The practical specific energy of Li₂S-Si (930 Wh/kg) is close to that of a Li-S battery (1000 Wh/kg).9 Second, because of its much higher melting/boiling points, Li₂S permits a wider temperature window for electrode fabrication.4 Third, Li₂S is fully lithiated, not requiring preset void space around Li₂S particles for accommodating the detrimental volume fluctuations that occur during the charge/discharge cycles.13, 14 Fourth, although a dry room or glovebox is required for electrode fabrication,9 Li₂S allows batteries to be assembled in the “discharged” state, a safer and more cost-effective process.8 Moreover, recently, scientists showed that the issues of poor electronic and ionic conductivity for Li₂S could be overcome by either applying a high activation potential or using nanoparticles.4, 9, 15 Therefore, Li₂S nanoparticles are highly
desirable for developing Li-S batteries; a large demand is expected in the near future. However, commercially, Li$_2$S is only available as micro-powders, reflecting high temperature processes used for industrial synthesis. The primary chemical reactions are listed below (4.1-4.3). Because lithium and sulfur both are very reactive at elevated temperatures, the operation of Reaction 4.1 is challenging, although it is a thermodynamically favorable reaction. An alternative way of running Reaction 4.1 is to dissolve lithium in liquid NH$_3$ at < -33 °C, but this approach brings additional complications. Reactions 4.2 and 4.3 are endothermic carbothermal reduction processes that require high temperatures and produce greenhouse gas. In addition, product purification in these three methods is also expected to be complicated and costly because at least one reactant is in the same phase as Li$_2$S.

$$\text{2Li + S} \xrightarrow{T \geq 300 ^\circ C} \text{Li}_2\text{S} \quad G_m^\circ(\text{Li}_2\text{S}) \approx -414 \text{ kJ/mol}$$ (4.1)

$$\text{Li}_2\text{SO}_4 + 2\text{C} \xrightarrow{T = 600 - 1000 ^\circ C} \text{Li}_2\text{S} + 2\text{CO}_2 \quad G_m^\circ(\text{Li}_2\text{S}) \approx +119 \text{ kJ/mol}$$ (4.2)

$$\text{Li}_2\text{CO}_3 + \text{H}_2\text{S} \xrightarrow{T = 600 - 1000 ^\circ C} \text{Li}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \quad G_m^\circ(\text{Li}_2\text{S}) \approx +120 \text{ kJ/mol}$$ (4.3)

Another drawback of current approaches is the size of the resulting powders (1 - 10 µm). It is commonly reported in the battery literature that nanostructured materials are superior to their bulk counterparts. Large surface/volume ratios promote thorough lithiation/delithiation (high (dis)charge capacity), fast diffusion (high rate capability), and mechanical resilience (high cycling stability). Current approaches to convert Li$_2$S micropowders into nanocrystals include ball milling, and recrystallization of dissolved Li$_2$S, but these approaches are both energy intensive and time consuming. A more elegant strategy would be direct synthesis of Li$_2$S nanocrystals. One approach being pursued is chemical/electrochemical lithiation of sulfur nanoparticles, but this multi-step process requires synthesis of well dispersed sulfur nanoparticles. Recently, two research groups reported direct syntheses of Li$_2$S nanocrystals by reacting lithium sulfate with carbon precursors at high temperatures (820 – 900 °C) for >2 hours. Elam et al. synthesized amorphous Li$_2$S nanofilms using a vapor-phase atomic layer deposition via alternating exposure to lithium tert-butoxide and hydrogen sulfide. However, it seems challenging for these methods to produce Li$_2$S nanocrystals at large scale.

This work reports a scalable, high throughput, room temperature approach to synthesizing Li$_2$S nanocrystals, by reacting hydrogen sulfide (H$_2$S) with lithium naphthalenide (Li-NAP), a thermodynamically spontaneous reaction that proceeds to completion rapidly at ambient pressure. The simple reaction directly generates Li$_2$S nanocrystals that precipitate out of solution, allowing easy recovery and purification. Because the value of Li$_2$S is many times higher than that of lithium, the cost of lithium
seems less likely to be a limiting factor for industrial production. Furthermore, ancillary benefits of this reaction include the removal of H₂S, a hazardous waste requiring abatement, and the production of 1,4-dihydronaphthalene, itself a value-added product with applications as an industrial solvent and a fuel additive. Electrochemical characterization of Li₂S nanocrystals synthesized in this work demonstrate its potential for use in Li-S batteries and advanced LIBs, outperforming commercial Li₂S micropowders, in terms of (dis)charge capacity, cycling stability, output voltage, and voltage efficiency.

4.4 Experimental Section

4.4.1 Chemicals

Lithium (Li) grains (ACS reagent, stick dry), naphthalene (NAP, C₁₀H₈, 99%), anhydrous 1,2-dimethoxyethane (DME, CH₃OCH₂CH₂OCH₃, 99.5%), hexanes (ACS grade), lithium ribbon (99.9% trace metals basis, 0.38 mm), bis(trifluoromethane)sulfonimide [LiTFSI, (CF₃SO₂)₂NLi, 99.95%], and tetra(ethylene glycol) dimethyl ether [TEGDME, CH₃O(CH₂CH₂O)₄CH₃, 99%] were purchased from Sigma-Aldrich. Lithium sulfide (Li₂S; 200 mesh, 99.9% metal basis) was purchased from Alfa Aesar. Anhydrous benzene-d₆ (C₆D₆, D-99.5%) was purchased from Cambridge Isotope Lab. Acetylene black (AB; 35–45 nm), anhydrous N-methylpyrrolidone (NMP, C₅H₉NO, >99.5%), poly(vinylidene fluoride) [PVDF, −(C₂H₂F₂)n−, >99.5%], and copper foil (99.99%, 9 μm) were purchased from MTI Corp. AB and PVDF were dried in a vacuum oven at 60 °C for 24 h before use. All other chemicals were used as received.

4.4.2 Synthesis of Li₂S

The first step is to make the 0.04 M lithium naphthalenide (Li-NAP) solution in DME by adding Li grains and NAP powder at a molar ratio of Li:NAP = 1:1.3 into DME in an argon-protected glovebox. A total of 2 h of stirring produced a dark green solution. After that, a Parr reactor (model 4793) was charged with 50 mL of the Li-NAP solution and connected to the H₂S stream (10% in argon). Figure 4.7 (page 59) illustrates the schematic diagram and photograph of the apparatus. Initially, the H₂S/Ar mixture at a rate of 40 sccm flowed through a bypass line at ambient temperature and pressure to create a baseline reading. Afterward, the H₂S/Ar stream was switched to the Li-NAP solution. An online quadrupole mass spectrometer (QMS; Stanford Research Systems RGA300) was employed to analyze the effluent. The molar ratio between Li-NAP and H₂S consumed was controlled by the H₂S-flowing duration.

Subsequently, in the glovebox, centrifugation was employed to separate the solid product out of the reaction solution. The collected solid powder was washed with DME a few times before being dried for further analysis. The production yield of Li₂S on the basis of lithium was about 95.6%, which was very satisfactory considering some loss of sample in the solution. The liquid phase was then concentrated via rotary evaporation to 1/5 of the original volume. The collected solution was kept in the glovebox for further analysis.
4.4.3 Products Characterization

X-ray diffraction (XRD) patterns were collected on a Philips X’Pert X-ray diffractometer using Cu Kα radiation (λ = 0.15405 nm). The sample was prepared in a glovebox by pressing the solid product into a thin film on a glass substrate. To avoid harmful reactions due to unavoidable air exposure during measurements, the solid was immediately covered with a drop of dried mineral oil in the glovebox. The background contribution from mineral oil was subtracted and corrected. Scanning electron microscopy (SEM) images were taken on a field-emission scanning electron micromter (JEOL JSM-7000F). The sample was prepared by immobilizing the obtained Li₂S powder on an aluminum stub using double-sided carbon tape. The accelerating voltage was 5 kV. Thermogravimetric analysis (TGA) was performed using a Q50 thermogravimetric analyzer (TA Instruments). The sample was prepared by pressing Li₂S powders into pellet inside an argon-filled glovebox. Before each run, the sample holder (an alumina pan) was cleaned by heating the furnace under air to 800 °C for 15 min. To eliminate the influence of physisorbed gases during sample preparation, samples were also preheated at 50 °C for 30 min before collecting the valid TGA data. The nitrogen flow rate for the balance compartment and the argon flow rate for the sample compartment were 40 and 60 mL/min, respectively. The temperature ramp rate was 2 °C/min.

The composition of the liquid supernatant produced by the reaction was analyzed by ¹H NMR (JEOL ECA-500) and gas chromatography–mass spectrometry (GC–MS). For NMR, 0.3 mL of the sample solution was dissolved in 0.2 mL of benzene-d₆ and loaded in a quartz sample tube. GC–MS analysis was conducted on a Varian CP3800 gas chromatograph coupled to a Varian 1200 L quadrupole mass spectrometer, for which the solid phase in the separation column is 5% diphenylpolysiloxane and 5% dimethylpolysiloxane. The precondition of the column was accomplished by injecting pure solvent DME at 320 °C. After that, the sample analysis was performed by injecting 1 μL of the sample solution with the column temperature at 250 °C. In both cases, the flow rates of the carrier gas of helium were 1.3 mL/min.

4.4.4 Electrode Fabrication and Electrochemical Analyses

Swagelok cell electrodes were fabricated to assess the electrochemical properties of the synthesized Li₂S. Electrode fabrication began by first drying the as-synthesized Li₂S powder under Ar in a tube furnace at 250 °C for 20 hours to completely remove the solvent DME and NAP used in the synthesis. After that, the dried Li₂S (40 wt%), AB (45 wt%), and PVDF binder (15 wt%) were blended manually in a mortar. The resultant mixture was dispersed in a small amount of NMP and stirred overnight. Next, the obtained slurry was bladed onto a carbon paper (AvCarbP50) collector and dried at 110 °C for 6 hours. Then, the electrodes were cut into small disks of 10 mm diameter using a compact precision disk cutter (MTI Corp., MSK-T-07). The mass loading of Li₂S was around 1.0 mg/cm². For benchmarking purposes, identical procedures were used to fabricate electrodes employing commercial Li₂S micropowders. Last, the half-cell batteries were assembled by using a lithium ribbon as the anode, a polypropylene membrane (Celgard 2500)
as the separator, and 1.0 M LiTFSI in TEGDME as the electrolyte. Cyclic voltammograms (CVs) were collected on a potentiostat (Princeton Applied Research, Versastat 4). The cycling stability was assessed via the galvanostatic technique at 0.1 C (1 C = 1166 mA/g), by using an eight-channel battery analyzer (MTI Corp., BST8-MA). The specific capacity was calculated according to the mass of Li$_2$S.

4.5 Results and Discussion

4.5.1 Demonstration of the Synthetic Method

On the basis of our previous work of abating H$_2$S with sodium naphthalenide (Na-NAP), the Li$_2$S-synthesis reaction is expected to be Equation 4.4 and will be verified step by step.

$$2\text{Li-C}_{10}\text{H}_{10} + \text{H}_2\text{S} \rightarrow \text{Li}_2\text{S} + \text{C}_{10}\text{H}_{10} + \text{C}_{10}\text{H}_8 \quad (4.4)$$

Figure 4.1A (page 47) plots the time evolution of signal intensities from the carrier gas argon (black), the solvent DME (blue), and the reactant H$_2$S (red) recorded by the online QMS, for a typical reaction using the stoichiometric molar ratio of Li-NAP:H$_2$S = 2:1. Initially, the H$_2$S/Ar mixture flowed through a bypass line to establish a baseline reading. When the bypass was closed at t = 127 s, both argon and H$_2$S fall exponentially with a time constant characteristic of the gas dynamics of the sampling apparatus. At t = 195 s the inlet and outlet valves of the reactor were opened simultaneously; and the argon signal immediately returns to its original value, accompanied by a step change in the signals associated with the volatile DME solvent. In stark contrast, the H$_2$S signal continues to exponentially decay, eventually dropping below the instrument’s detection limit. This indicates that the H$_2$S supplied has been consumed at least 99.9%. The mass spectrum recorded from the effluent (Figure 4.1B, red) shows no signals of H$_2$S across the mass/charge (m/z) range of 32–34, while that recorded from the bypass mode (Figure 4.1B, black) shows the expected signals of H$_2$S evidently. Thus, the consumption of H$_2$S through its reaction with LiNAP is demonstrated to be spontaneous, complete, and nearly instantaneous, as previously observed for the Na-NAP systems.

As shown in Figure 4.1C (red), the XRD pattern of the obtained solid product is well consistent with that of the Li$_2$S standard (black), indicating the successful generation of anhydrous, phase-pure, crystalline Li$_2$S. According to the Scherrer equation, which correlates crystalline domains with the peak width, Li$_2$S crystals are ~5 nm in diameter. The SEM image (Figure 4.1D) shows that Li$_2$S nanocrystals aggregate as secondary particles of ~100 nm.

The $^1$H-NMR NMC spectrum of the liquid phase, obtained by using benzene-d$_6$ as the solvent, is shown in Figure 4.2A (page 48). Besides the expected DME, benzene, and NAP, three weak peaks at 6.91 - 5.66 pm are assigned to the hydrogen atoms at positions a and b of 1,4-dihydronaphthalene. The signal of the hydrogen atoms at position c is expected to show up at
3.3–2.9 ppm but is masked by the intense signal of DME. The chromatogram recorded by GC–MS (Figure 4.2B) shows two peaks. The corresponding MS spectra can be indexed to 1,4-dihydronaphthalene and NAP, respectively.\textsuperscript{39, 40} Thus, the characterization results shown in Figures 4.1 and 4.2 prove that the Li\textsubscript{2}S synthesis follows Equation 4.4, as previously observed for the Na-NAP systems.\textsuperscript{35} Note that this synthetic method enables facile operation/separation because the reactants and products exist in different phases.

![Figure 4.1](image1.png)

**Figure 4.1** Characterization of the reaction for synthesizing Li\textsubscript{2}S nanocrystals. (A) Time evolution of QMS to monitor the concentrations of key species in the gas phase: argon (black); H\textsubscript{2}S (red); DME (blue). (B) MS spectra in the window of m/z 30–35 for the gaseous effluents through the bypass (black) and through the reactor (red). (C) XRD pattern of the obtained solid product (red) together with the stick pattern (black) of the Li\textsubscript{2}S standard (JCPDS 04-003-6927). (D) SEM image of the obtained solid product.

Then, we tested the effect of molar ratio of Li-NAP/H\textsubscript{2}S on the Li\textsubscript{2}S synthesis (Figure 4.8 on page 59) At the ratios of 3:1 and 1.5:1, the solid products were also phase pure anhydrous Li\textsubscript{2}S nanocrystals with comparable sizes and shapes in the case of the stoichiometric 2:1. Differently, in the case of 1:1, which was expected to produce LiHS, no solid product was observed in the reaction system. After evaporation the solvent, only a gel-like substance was obtained, showing no sign of crystals. \textsuperscript{1}H NMR did not produce any meaningful signals that could be assigned to known compounds. We believe that this is because LiHS fully dissolves in DME and exists in some unknown complex form. For example, it is known that LiHS cannot precipitate out of ethanol but forms a LiHS/ethanol complex.\textsuperscript{41} The comparison with our previous work indicates that LiHS has higher solubility/complexity in DME than NaHS.\textsuperscript{35} These results demonstrate
the robustness of this synthetic method to produce phase-pure Li$_2$S nanocrystals, and for practical operation, the use of stoichiometric mixture is ideal to fully consume H$_2$S while maximizing the conversion of lithium to Li$_2$S.

![Figure 4.2](image)

**Figure 4.2** Characterization of the liquid phase collected from the synthetic reaction: (A) the $^1$H NMR spectrum; (B) the gas chromatogram; (C) MS spectrum for peak 1 in part B; (D) MS spectrum for peak 2 in part B.

### 4.5.2 Structural and Electrochemical Analyses

The synthesized Li$_2$S nanocrystals (denoted as s-Li$_2$S) were further characterized after drying to remove residual organics. The TGA plots in Figure 4.3A (page 49) shows that s-Li$_2$S (red) has a purity comparable to that of the commercial Li$_2$S micropowders (denoted as c-Li$_2$S, blue), as indicated by their nearly identical weight loss profiles, of which the overall difference is only 1%. We speculate that the abrupt weight loss at about 400 °C is likely to result from the decomposition of some unknown impurities, because the melting point of pure Li$_2$S is above 900 °C. Possible culprits include lithium hydroxide (LiOH), hydrogen sulfide (H$_2$S), and lithium carbonate (Li$_2$CO$_3$), which could be formed via the reaction between trace amounts of H$_2$O and CO$_2$ with Li$_2$S during sample storage and handling in the glove box and environment. The slight weight increase before 400 °C may be ascribed to the reaction of Li$_2$S with trace amounts of H$_2$O, O$_2$, and/or CO$_2$ in the carrier gas, which results in greater reaction in the case of s-Li$_2$S due to its larger surface/volume ratio than c-Li$_2$S. XRD patterns in Figure 4.3B indicate a slight growth of the crystalline sizes for s-Li$_2$S from the original 5 nm to the present 20 nm after heat treatment, according to the Scherrer equation, but still much smaller than that of c-Li$_2$S (50 nm). Note that the
estimated crystalline sizes denoted here provide a lower bound and are primarily used as a relative comparison among the different Li$_2$S materials because use of the Scherrer equation assumes that the nanosize effect is the only (or predominant) factor in peak broadening. The crystal growth of s-Li$_2$S during annealing is also corroborated by the SEM image in Figure 4.3C, which include more secondary particles without clear boundaries among nanocrystals. In contrast, c-Li$_2$S exist mainly as irregular microparticles of about 1 - 5 µm diameter with some smaller particles of about 100 nm, as shown in Figure 4.3D.

The electrochemical properties of both s-Li$_2$S and c-Li$_2$S were examined in half cells according to the slurry protocol described in the experimental section. Part A and B of Figure 4.4 (page 51) show the first four cycles of the CVs of s-Li$_2$S and c-Li$_2$S, respectively. The observed results are consistent with the typical behavior of Li-S batteries reported in the literature. As is widely known, the material’s speciation cycles between two extreme states of sulfur (S$_8$) at 1.5 V and Li$_2$S at 3.0 V through Reactions 4.5–4.9.

\[ 2\text{Li}^+ + 2\text{e}^- + \text{S}_8 \rightleftharpoons \text{Li}_2\text{S}_8 \]  

(4.5)
\[2\text{Li}^+ + 2e^- + 3\text{Li}_2\text{S}_8 \leftrightarrow 4\text{Li}_2\text{S}_6 \]  \hspace{1cm} (4.6)

\[2\text{Li}^+ + 2e^- + 2\text{Li}_2\text{S}_6 \leftrightarrow 3\text{Li}_2\text{S}_4 \]  \hspace{1cm} (4.7)

\[2\text{Li}^+ + 2e^- + \text{Li}_2\text{S}_4 \leftrightarrow 2\text{Li}_2\text{S}_2 \]  \hspace{1cm} (4.8)

\[2\text{Li}^+ + 2e^- + \text{Li}_2\text{S}_2 \leftrightarrow 2\text{Li}_2\text{S} \]  \hspace{1cm} (4.9)

In the case of s-Li\(_2\)S, the initial open circuit potential (OCP; 2.40 V vs Li/Li\(^+\)) that lies between 3.0 and 1.5 V can be ascribed to the self-delithiation of Li\(_2\)S to lithiate the carbon additive, whose OCP is about 2.9 V.\(^{46}\) In the first half cycle, the anodic current with a weak peak at 2.57 V (peak I) corresponds to the delithiation of Li\(_2\)S to form sulfur.\(^{11,24}\) In the subsequent cathodic scans, three characteristic peaks are observed at ca. 2.44 V (peak II, strong), ca. 2.12 V (peak III, weak) and 1.94 V (peak IV, very strong), respectively.\(^{11,24}\) Peak II is typically assigned to the reduction of S\(_8\) to polysulfides (Li\(_2\)S\(_n\), where n = 4 – 8) in three steps (Equations 4.5 – 4.7). Peak III is believed to result from the reduction of Li\(_2\)S\(_4\) to insoluble Li\(_2\)S\(_2\) (Equation 4.8).\(^{11}\) Peak IV is due to the conversion of Li\(_2\)S\(_2\) to Li\(_2\)S (Equation 4.9).\(^{11}\) In contrast, the subsequent anodic scans only have two distinguishable peaks at 2.39 V (peak V) and 2.53 V (peak VI), which correspond to the oxidation of Li\(_2\)S first to polysulfides and subsequently to S\(_8\), respectively. The steady peak potentials and current intensities during the illustrated cycles in Figure 4.4A manifest the good stability and reversibility of the s-Li\(_2\)S electrode. The electrochemistry of the commercial c-Li\(_2\)S is quite similar because the six peaks just described are readily identified (Figure 4.4B). The prominent difference between the two materials is their stability. In the case of c-Li\(_2\)S, the anodic (cathodic) peaks shift more positive (negative) and the current intensities consecutively increase over the first few cycles, indicating the inferiority of c-Li\(_2\)S to s-Li\(_2\)S in electrolyte wettability and electrochemical reversibility.\(^{47}\)

The galvanostatic technique was employed to assess the cycling stabilities (Figure 4.5 on page 51) of s-Li\(_2\)S (red) and c-Li\(_2\)S (blue) electrodes in both the charge (solid circles and squares) and discharge (open circles and squares) processes. s-Li\(_2\)S is superior to c-Li\(_2\)S in all regards. The initial charge (delithiation) and discharge (lithiation) capacities for s-Li\(_2\)S are 724 and 669 mAh/g, respectively, which compares well with the theoretical limit of 1166 mAh/g considering that electrode fabrication was not optimized.\(^{4}\) The performance gradually declines, and the half-life, defined as the cycles spent to reach 50% of the initial charge capacity, is 45 cycles for s-Li\(_2\)S. Because Li\(_2\)S is in the fully lithiated state, the Coulombic efficiency (CE) is defined as the ratio of lithiation (discharge) capacity to the delithiation (charge) capacity.\(^{48}\) The s-Li\(_2\)S displayed 92% CE in the first cycle and then quickly increased to 98 – 100% in all subsequent cycles.
Figure 4.4 Typical CVs in the first four cycles of s-Li$_2$S (A) and c-Li$_2$S (B), where the scan rate is 0.1 mV/s.

Figure 4.5 Typical plots of specific capacity in charge (solid circles and squares) and discharge (open circles and squares) processes and coulombic efficiency (solid diamonds) versus cycle number for both s-Li$_2$S (red) and c-Li$_2$S (blue), for which the galvanostatic current is 116.6 mA/g (0.1 C, 1C = 1166 mA/g).

In contrast, the initial charge capacity of the c-Li$_2$S is only 272 mAh/g. The subsequent discharge capacity contributes 356 mAh/g, resulting in a “abnormally” high CE (CE = 356 / 272 = 131%), which may be ascribed to the compensation for the loss of Li due to self-delithiation before the measurement and the dissolution of polysulfides during the discharge process, as pointed out in the literature. In the second cycle, the charge capacity bounces to 424 mAh/g. The CE values in the subsequent cycles are comparable with those of s-Li$_2$S. The stability c-Li$_2$S declines in a similar fashion but reaches its half-life after only 23 cycles. The differences in the initial CE and stability suggest that s-Li$_2$S particles, compared with c-Li$_2$S particles, are better protected by the additives used in electrode fabrication because of their smaller particle sizes. Moreover, s-Li$_2$S herein also performs significantly better than c-Li$_2$S in the literature (630 mAh/g for the initial capacity and 240 mAh/g at the 30th cycle).
Despite no optimization of the electrode fabrication procedure, the performance of s-Li$_2$S synthesized in this work compares favorably with some s-Li$_2$S particles in the literature. For instance, the Li$_2$S-C nanocomposite made by reacting lithium sulfate with resorcinol/formaldehyde showed an initial capacity of 350 mAh/g and 300 mAh/g at the 30th cycle; the Li$_2$S-C nanocomposite made by thermally annealing a mixture of polysulfide Li$_2$S$_3$ and polyacrylonitrile exhibited the specific capacity of 500 mAh/g initially and 500 mAh/g at the 20th cycle; the Li$_2$S-C nanocomposite made by ball-milling Li$_2$S micropowder and carbon precursor presented the specific capacity of 560 mAh/g initially and 420 mAh/g at the 30th cycle. s-Li$_2$S synthesized in this work displays significantly higher initial (dis)charge capacity but inferior cycling stability. It is expected that the latter issue can be addressed through the optimization of electrode fabrication procedures, by following published strategies in the literature a topic of our future work.

As shown in Figure 4.6 (page 53), s-Li$_2$S and c-Li$_2$S present different potential profiles in the first half cycle (black). With respect to s-Li$_2$S, as highlighted by the inset of Figure 4.6A, a small potential barrier between 2.46 V and 2.52 V is overcome to contribute the initial delithiation capacity of 50 mAh/g. After that, only one plateau at 2.42 V is observed to contribute the remaining 670 mAh/g before sharply rising to the cutoff potential 3.0 V. In contrast, the potential profile of c-Li$_2$S (Figure 4.6B, black) exhibit a flat plateau at 2.50 V for the initial 200 mAh/g and a sloping plateau between 2.8 V and 3.0 V for the remaining 70 mAh/g. The first plateau can be considered to be a consequence of encountering a continuous potential barrier.

The potential profile of s-Li$_2$S described above confirms that this material does not require a significant potential to activate its charge capacity, consistent with literature reports for Li$_2$S nanoparticles. However, Li$_2$S micropowders reported in the literature require one to overcome a large activation barrier in the range of 3.5 and 4.0 V. The activation process contributes only 48 mAh/g, while the subsequent plateau at 2.5 V can contribute as high as 600 mAh/g. Thus, our c-Li$_2$S electrode seems to behave partially like Li$_2$S nanoparticles and partially like Li$_2$S microparticles. When referring to our XRD result (which shows the crystalline sizes of c-Li$_2$S to be ≥ 50 nm) and SEM observation (some particles are around 100 nm) in Figure 4.3 (page 49), we speculate that the capacity observed in the c-Li$_2$S electrode be predominantly from those nano/submicroparticles; microparticles seem barely activated because of the requirement of higher cut-off potentials.
Figure 4.6 Several cycles of voltage profiles against the specific capacity for s-Li$_2$S (A) and c-Li$_2$S (B), where the inset in (A) highlights the activation period in the first cycle.

The potential profiles in the subsequent cycles corroborate the lithiation/delithiation mechanism described in the discussion of the cyclic voltammetry results (Figure 4.4 on page 51). Both s-Li$_2$S and c-Li$_2$S show three distinguishable plateaus during the discharge processes and two plateaus during the charge processes. For s-Li$_2$S (Figure 4.6A), the discharge plateaus are at 2.45 V (Equations 4.5-4.7), 2.2 V (Equation 4.8), and 2.06 V (Equation 4.9); the charge plateaus are at 2.25 V (Equations 4.8-4.9), and 2.50 V (Equations 4.5-4.7). All these values except 2.06 and 2.25 V are essentially consistent with the corresponding peak potentials in the CV (Figure 4.4A). The small differences in the positions of these two peak potentials between the galvanostatic and cyclic voltammetric processes (2.06 V vs 1.94 V and 2.25 V vs 2.39 V) can be explained by the different reaction kinetics and polarization effects. In the case of c-Li$_2$S (Figure 4.6B), while the charge plateau (2.25 V) is the same as that of s-Li$_2$S, the discharge plateau (2.02 V) is slightly lower, which means that, in principle, s-Li$_2$S could provide higher energy and power densities than c-Li$_2$S. Moreover, it is worth noting that the potential hysteresis between the charge plateau (2.25 V) and the discharge plateau (2.06 V) for the s-Li$_2$S electrode herein is only 0.19 V (lower than the 0.23 V for c-Li$_2$S), comparable with the smallest value reported in the literature (0.2 V),$^{12}$ where most values are in the range of 0.25 – 0.4 V.$^{4,9,11}$ Small hysteresis is desirable and indicative of high voltage efficiency.

The electrochemical analyses above show that the s-Li$_2$S nanocrystals synthesized from reacting H$_2$S with Li-NAP hold promise as electrode materials for advanced rechargeable batteries. They are superior to commercial c-Li$_2$S in (dis)charge capacity, cycling stability, output voltage, and voltage efficiency. Despite simple electrode fabrication procedures, their performance is already comparable with some s-Li$_2$S materials reported in the literature.

4.6 Conclusion

In conclusion, we have demonstrated a new method of synthesizing anhydrous Li$_2$S nanocrystals and confirmed their promise as potential cathode materials for Li-S batteries and advanced LIBs. The synthesis is realized by reacting Li-NAP with H$_2$S, a thermodynamically spontaneous reaction at ambient
temperature and pressure that is fast, complete, and irreversible. Compared with the commercial Li$_2$S micropowders (1-5 µm), the synthesized Li$_2$S nanocrystals (100 nm) present superior performance in all regards, including (dis)charge capacity, cycling stability, output voltage, and voltage efficiency. These results clearly manifest the potential of this synthetic method for practical production of high-quality Li$_2$S nanoparticles because it is conducted at mild conditions and Li$_2$S is the only solid phase, facilitating separation and purification. Work is in progress to improve battery performance through optimization of electrode fabrication and by tuning the morphology of Li$_2$S nanocrystals through judicious choice of alternative complexing reagents and solvents.

4.7 Associated Content

Supporting Information: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b09367. Schematic diagram and photograph of the apparatus as well as XRD patterns and SEM images of Li$_2$S produced by using different molar ratios of Li-NAP/H$_2$S.

4.8 Author Information

Author Contributions: The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding: This work is financially supported by the Startup Fund for Y.Y. from the Colorado School of Mines. C.A.W. acknowledges support by the National Science Foundation through award DMR-1207294. C.B. acknowledges support by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, Subcontract No. DE-AC-36-08GO28308 under Exploratory Battery Materials Research program.

Notes: The authors declare no competing financial interest.

4.9 Acknowledgements

We are thankful to Professor Yuan Yang for her helpful advices on NMR measurements.

4.10 References


(38) "Japan National Institute of Advanced Industrial Science and Technology (AIST), Spectral Database for Organic Compounds, S.D.B.S.".


(40) NIST-MS-Search, NIST14 and Wiley Databases. NIST-MS-Search, NIST14 and Wiley databases 2014.


4.11 Supporting Information

Figure 4.7 Schematic diagram (A) and photograph (B) of the reaction apparatus used for synthesizing Li$_2$S.

Figure 4.8 XRD patterns (A and C) and SEM (B and D) characterization of the solid products out of two reactions that are conducted at the molar ratio of Li-NAP:H$_2$S = 3:1 (A and B) and 1.5:1 (C and D).
5.1 Abstract

Anhydrous alkali sulfide (M$_2$S, M = Li and Na) nanocrystals (NCs) are important materials central to the development of next generation cathodes and solid state electrolytes for advanced batteries. This work reports an innovative method to directly synthesize M$_2$S-NCs through alcohol-mediated reactions between alkali metals and hydrogen sulfide (H$_2$S). In the first step the alkali metal is complexed with alcohol in solution, forming metal alkoxide (ROM) and releasing hydrogen (H$_2$). Next, H$_2$S is bubbled through the ROM solution, where both chemicals are completely consumed to produce phase-pure M$_2$S-NC precipitates and regenerating alcohol that can be recycled. The M$_2$S-NC morphology may be tuned through choice of the alcohol and solvent. Both synthetic steps are thermodynamically favorable ($\Delta G_m^o < -100$ kJ/mol), proceeding rapidly to completion at ambient temperature with ~100% atom efficiency. The net result, H$_2$S + 2M $\rightarrow$ M$_2$S + H$_2$, provides abatement of the hazardous industrial waste H$_2$S and delivers two value-added products that naturally phase separate for easy recovery. This scalable approach provides an energy-efficient and environmentally-benign solution to the production of nanostructured materials required in emerging battery technologies.

5.2 Keywords

Alkali Sulfides; Hydrogen Sulfide; Nanocrystal Synthesis; Battery Materials; Hydrogen Generation.

5.3 Broader Context

The world is striving to develop a sustainable future. Renewable generation of electricity is expanding rapidly, but full market penetration requires efficient and cost-effective technologies for energy conversion and storage. With lithium ion batteries (LIBs) approaching performance limits it is imperative to develop more advanced systems. Leading candidates to displace LIBs include metal-sulfur batteries (M-S, M = Li and Na) and solid-state batteries. Both systems require anhydrous M$_2$S nanocrystals, currently produced through energy intensive carbo-thermal reduction processes in concert with time-consuming ball milling. This article describes a green chemistry-inspired approach for the direct synthesis of M$_2$S nanostructures by reactive precipitation. This solution-based strategy is scalable and flexible, as the size and shape of the resulting nanocrystals may be engineered through appropriate selections of the solvent and the alcohol. Complementary attributes include abatement of the hazardous waste hydrogen sulfide, recovery of the valuable hydrogen stored within, and recycling/reuse of the organic solution. The thermodynamically
favorable reactions rapidly proceed to completion at ambient temperature without additional energy input. The synergistic combination of nanocrystal synthesis, H$_2$S abatement, and H$_2$ generation presents an environmentally-friendly process for scalable manufacturing of nanomaterials that will enable next generation battery technologies.

5.4 Introduction

Solar and wind generation of electricity are commercialized and growing steadily, with new installations exceeding 50 GW/year. Efficient technologies for storage and deployment are required to adapt the temporal nature of these sources to match consumption and ensure their continued expansion. Lithium ion batteries (LIBs) are a well-developed energy storage system, but they are approaching intrinsic performance limits and cannot meet the demands required for electric vehicles (EVs), advanced consumer electronics, and stationary storage. Leading candidates to supplant LIBs include solid state batteries and those based on the lithium-sulfur (Li-S) redox pair. Solid state batteries employ conventional electrode materials (i.e. graphite/LiCoO$_2$), but may achieve 2 - 3 times higher energy density than LIBs by replacing the volatile and flammable liquid electrolyte with a solid electrolyte (SE). Sulfide ceramics derived from lithium sulfide (Li$_2$S) are prominent SE materials owing to their high conductivity and superior ductility, with leading candidates based on the Li$_2$S-P$_2$S$_5$ and Li$_2$S-GeS$_2$ systems.

Li-S batteries are particularly attractive for EV applications, due to their high practical specific energy, long driving distance, and low pack prices. Room temperature Na-S batteries, which have similar working principles as Li-S batteries, are also highly attractive for stationary storage due to the abundance and low cost of Na. While the simplest configuration for M-S batteries employs a M (M = Li and Na) anode and a S cathode, the use of alkali metal sulfide (M$_2$S, M = Li and Na) cathodes present several advantages. First, M$_2$S cathodes can also be paired with metal-free anodes, such as existing anodes (graphite) or emerging materials (Si and Sn). For example, the practical specific energy of Si-Li$_2$S (930 Wh/kg) is close to that of Li-S batteries (1000 Wh/kg). Second, M$_2$S cathodes are fully lithiated, not requiring preset void space around M$_2$S particles for accommodating the detrimental volume fluctuations that occur during charging/discharging cycles. Third, the electrode fabrication is simple due to the greater thermal stability of M$_2$S, and it allows batteries to be assembled in the discharged state, a safer and more cost-effective process. Emerging solid state battery architectures incorporate M$_2$S into all three components: cathode, anode and electrolyte, demonstrating the great importance of M$_2$S for solid state batteries.

Despite these benefits, M$_2$S electrodes confront some shared challenges with sulfur electrodes. First, M$_2$S in the bulk form is a very poor electronic and ionic conductor, requiring the use of large overpotentials to initiate cycling. Second, charging/discharging proceeds through polysulfide intermediates (M$_2$S$_n$, n = 4 - 8) which have high solubility in conventional electrolyte solutions and migrate...
between the cathode and the anode.\textsuperscript{23} This can lead to a serious loss of active material and anode corrosion.\textsuperscript{15, 20, 24, 25}

To address these issues the scientific community has invested significant effort in recent years to develop nanocrystal (NCs)-based cathodes.\textsuperscript{7, 8, 16-18, 26-29} Compared with bulk materials, the high specific surface area of NCs enables higher cycling stability, specific capacity, and rate capability.\textsuperscript{22, 30} In addition, the high activation potential required for bulk materials is not needed for NCs.\textsuperscript{18, 29} Nanostructure is equally important for producing high quality M\textsubscript{2}S-based solid electrolytes. The fabrication of ceramic electrolytes involves mixing and annealing (200-600 °C) the constituent nanopowders (M\textsubscript{2}S, P\textsubscript{2}S\textsubscript{5}, and GeS\textsubscript{2}).\textsuperscript{8, 9} It has been shown that reducing the particle size of M\textsubscript{2}S improves the reversible capacity of all-solid-state cells due to the higher electrolyte conductivity and the reduced resistance at the electrolyte-electrode interface.\textsuperscript{7} In addition, reductions in particle sizes are beneficial for lowering the thermal budget required in subsequent annealing treatments.

Unfortunately, phase pure M\textsubscript{2}S nanocrystals are commercially unavailable at present. Bulk M\textsubscript{2}S is mainly produced by high temperature processes.\textsuperscript{31-34} One method is to react molten metal with sulfur at a temperature higher than 300 °C, requiring high quality of reaction container.\textsuperscript{33} Another method is to react metal hydroxide (MOH) with H\textsubscript{2}S at high temperature, producing M\textsubscript{2}S and H\textsubscript{2}O which are not compatible with each other.\textsuperscript{31} The most commonly used approach is carbothermal reduction of metal sulfate (M\textsubscript{2}SO\textsubscript{4}), with the disadvantages of carbon dioxide emission.\textsuperscript{32} The high temperatures employed in these processes yield M\textsubscript{2}S in the form of micropowders, and impurities are a major concern. Additionally, Na\textsubscript{2}S is most commonly available in its hydrate form (Na\textsubscript{2}S·xH\textsubscript{2}O, x\textasciitilde 9) and contains polysulfide impurities. At present, the lack of M\textsubscript{2}S-NC suppliers puts significant constraints on battery manufacturers that would like to integrate M\textsubscript{2}S-NCs into their products. The most common strategy is to convert commercial M\textsubscript{2}S micropowders into M\textsubscript{2}S-NCs through high energy ball milling,\textsuperscript{7, 18, 27, 35} which is time consuming and can introduce additional impurities. Other methods demonstrated in academia include recrystallization of dissolved M\textsubscript{2}S,\textsuperscript{26, 28, 29, 36} (electro)chemical lithiation/sodiation of sulfur NCs,\textsuperscript{17, 37-39} or carbothermal reduction using molecular carbon precursors.\textsuperscript{32, 40} The challenges for all of these approaches are that they are energy intensive, time consuming, and not amenable to scale-up.

The goal of this work was to develop an environmentally benign alternative for direct synthesis of pure and anhydrous M\textsubscript{2}S-NCs. The ideal chemistry underlying our proposed approach for the scalable manufacturing of M\textsubscript{2}S nanostructures is shown in Figure 5.1 (page 63). Anhydrous, phase pure M\textsubscript{2}S-NCs can be generated through the reaction between hydrogen sulfide (H\textsubscript{2}S) and alkali metals introduced in the form of metalorganic complexes (R-M) dissolved in solutions. This reaction is thermodynamically favourable (ΔG\textsubscript{m°} << 0 kJ/mol), and it proceeds to completion instantly and irreversibly at ambient temperature. In the ideal process, valuable hydrogen (H\textsubscript{2}) can be recovered during the regeneration of R-
M complex, realizing the net reaction of $\text{H}_2\text{S} + 2\text{M} \rightarrow \text{M}_2\text{S} + \text{H}_2$.

Figure 5.1 Proposed chemical pathway for the efficient and sustainable M$_2$S manufacturing.

This process exhibits many attributes of green chemistry\textsuperscript{41} and engineering.\textsuperscript{42} First, lithium is the critical element and the major cost driver in advanced battery technologies and must be used efficiently. The proposed chemistry proceeds with an atom economy approaching 100%, meaning that the M and H$_2$S supplied are completely converted into M$_2$S and H$_2$. Second, H$_2$S is a dangerous pollutant and health hazard that represents a major liability for oil and gas production. Our process results in complete H$_2$S abatement, and may contribute as part of a comprehensive solution to this industrial waste problem. Another green principle is that the process is designed for separation, since the solid (M$_2$S) and vapor-phase (H$_2$) products are produced in different steps and readily separated from the solution that can be recycled/regenerated. Lastly, this process requires no thermal energy input. The combination of hazardous waste removal (H$_2$S), co-generation of valuable byproducts (H$_2$) and the absence of significant energy requirements in all stages of synthesis, product separation, and recycling of auxiliary reagents, suggests that at scale this process should be able to generate M$_2$S-NCs without significant additional costs beyond that of the metal reagent.

The first demonstration of this process was accomplished using naphthalene (NAP, C$_{10}$H$_8$) as the organic mediating reagent R, which worked equally well for generating both Na$_2$S and Li$_2$S NCs as detailed in our two recent publications.\textsuperscript{43, 44} In both cases the reaction proceeded as Reaction 5.1. Reaction 5.1 was found to be spontaneous, rapid, and complete at room temperature, reducing H$_2$S in the effluent below detection limits with the successful synthesis of pure M$_2$S-NCs.\textsuperscript{43, 44} The yield of M$_2$S-NCs based on the initial mass of metal used was as high as 96%. The results using naphthalene were very encouraging, but a few aspects could be further improved. First, hydrogen was not directly released but captured in the form of 1,4-hydrogennaphthalene (1,4-C$_{10}$H$_{10}$, commonly known as 1,4-dialin). Although 1,4-dialin has added value as a solvent, recovering H$_2$ directly would be highly desirable for industrial applications. Moreover, recycling/regeneration of the organic reagent as depicted in Figure 5.1 was not straightforward in the naphthalene system.

$$2\text{M-C}_{10}\text{H}_8 + \text{H}_2\text{S} \rightarrow \text{M}_2\text{S} + 1,4\text{-C}_{10}\text{H}_{10} + \text{C}_{10}\text{H}_8$$ (5.1)
In this paper, we will demonstrate the idealized process of Figure 5.1 (page 63) by replacing naphthalene with alcohols as the mediating reagents. The M₂S-NC synthesis and H₂S abatement are accomplished in one step with the H₂ recovery and reagent regeneration occurring in the second, as expressed by Reactions 5.2-4. In the first step (Reaction 5.2) M₂S-NCs precipitate from the reaction of H₂S with a metal alkoxide (ROM) precursor, regenerating the alcohol mediator (ROH). After collecting the NCs by centrifugation, the solution is reacted with fresh alkali metal to regenerate the metal alkoxide precursor and release H₂ (Reaction 5.3). In this paper, we first demonstrate and quantify the individual process steps using reactive precipitation of Na₂S from sodium ethoxide (EtONa) in ethanol/1,2-dimethoxyethane (EtOH/DME) as a model system. Then we demonstrate the flexibility of the process to engineer the morphology of M₂S NCs through appropriate selection of various alcohol/solvent combinations. The development of high performance M₂S cathodes, which requires extensive engineering of the electrode fabrication (such as carbon encapsulation with hierarchical structures) and systematic electrochemical characterizations, is in progress and will be published separately.

\[
\begin{align*}
\text{H}_2\text{S} (g) + 2\text{ROM} (\text{sln}) & \xrightarrow{RT, 1 \text{ atm}} \text{M}_2\text{S} (s) + 2\text{ROH} (l) \quad \Delta G_m^o \approx -116 \text{ kJ/mol} \quad (5.2) \\
2\text{M} (s) + 2\text{ROH} (\text{sln}) & \xrightarrow{RT, 1 \text{ atm}} 2\text{ROM} (\text{sln}) + \text{H}_2 (g) \quad \Delta G_m^o \approx -265 \text{ kJ/mol} \quad (5.3) \\
2\text{M} (s) + \text{H}_2\text{S} (g) & \xrightarrow{RT, 1 \text{ atm}} \text{M}_2\text{S} (s) + \text{H}_2 (g) \quad \Delta G_m^o \approx -381 \text{ kJ/mol} \quad (5.4)
\end{align*}
\]

5.5 Experimental Section

5.5.1 Chemicals

Sodium (Na, ACS reagent, stick dry), ethanol (EtOH, CH₃CH₂OH, anhydrous, containing 5% isopropyl alcohol, 5% methyl alcohol), 1-butanol (butanol, CH₃(CH₂)₂OH, anhydrous, 99.8%), 1-hexanol (hexanol, CH₃(CH₂)₅OH, anhydrous, ≥99%), 1-octanol (octanol, CH₃(CH₂)₇OH, anhydrous, ≥99%), 1,2-dimethoxyethane (DME, CH₃OCH₂CH₂OCH₃, anhydrous, 99.5%), 2-methyltetrahydrofuran (2-MeTHF, C₅H₁₀O, anhydrous, ≥99%), 1,4-dioxane (dioxane, C₄H₈O₂, anhydrous), dibutyl ether (DBE, CH₃(CH₂)₃O, anhydrous, 99.3%), toluene (C₆H₅CH₃, anhydrous, 99.8%) and hexane (C₆H₁₂, anhydrous, ≥99%) were purchased from Sigma-Aldrich. Lithium foil (Li, 99.9% trace metals basis, 0.75 mm thick × 19 mm wide) was purchased from Alfa Aesar. Anhydrous benzene-D₆ (C₆D₆, D-99.5%) was purchased from Cambridge Isotope Lab. Sodium sulfide nonahydrate (Na₂S·9H₂O, ≥98.0 %) was purchased from Fisher Scientific. Dioxane was treated using Na metal to remove trace amount of water before use. All other chemicals were used as received.
5.5.2 Synthesis of Na$_2$S and Li$_2$S

Appropriate amounts of alcohol (ROH = ethanol, butanol, or hexanol) and alkali metal (Na or Li) were sequentially added into 40 mL solvent (DME, 2-MeTHF, dioxane, DBE, toluene or hexane) in an Ar-filled glove box (MBraun LABstar MB10 compact) to make a 0.05 M metal alkoxide (ROM) solution. The molar ratio of ROH to M was 8, and it took about two hours to fully dissolve the metal. Then, the prepared ROM solution was placed in a Parr reactor (model 4793). After that, the reactor was connected to the gas line containing 10 atom% of H$_2$S in the carrier gas Ar, which can be changed to N$_2$ for larger scale of synthesis to save costs. The schematic diagram of the apparatus is shown in Figure 5.2A (page 67). Initially, the H$_2$S/Ar mixture at the rate of 40 sccm flowed through a bypass line to establish a baseline reading. Then, the bypass was closed and the H$_2$S/Ar flow was diverted into the Parr reactor to react with the ROM solution at ambient temperature and pressure. The effluent was evacuated using a vacuum pump and detected in line using a differentially pumped quadrupole mass spectrometer (QMS, Stanford Research Systems RGA300). The overall molar ratio of ROM to H$_2$S supplied to the reactor was fixed at the stoichiometric 2:1 ratio, controlled by the duration of the gas flow into the reactor. At the end of the reaction, the reactor inlet and outlet valves were closed simultaneously. Finally, the reactor was transferred into the Ar-filled glove box. The reaction solution was centrifuged to separate the liquid phase and the solid phase. The solid phase was washed several times with the solvent used in the respective reaction and dried on a hot plate at 80 °C in the glovebox. The liquid phase from the model reaction of EtONa-EtOH/DME was also saved for further characterization.

5.5.3 Product Characterization

X-ray diffraction (XRD) patterns were collected on a Philips X’Pert X-Ray diffractometer using Cu K$_\alpha$ radiation (λ = 0.15405 nm). The samples were prepared in the Ar-filled glove box by spreading sample powders onto glass substrates. A drop of mineral oil was used to cover the sample to prevent detrimental reactions with moisture in air during the measurements. The background contributed from the mineral oil (a smooth and broad peak centered at 17.2° spanning from 10 to 25°) was subtracted. Field emission scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were collected on JEOL JSM-7000F FESEM, which is equipped with a JEOL EDAX detector. The SEM sample was prepared by immobilizing the synthesized solid product on an aluminum stub using a double-sided carbon tape. The accelerating voltage was 5 kV and 15 kV for taking SEM images and EDX spectra, respectively. Thermogravimetric analysis (TGA) was performed using a Q50 TGA (TA Instruments), for which the pellet-shaped samples were prepared via cold-pressing inside the Ar-filled glovebox. Before each TGA run, the sample holder (an alumina pan) was cleaned by heating in the furnace under air at 800 °C for 15 minutes. To eliminate the influence of physisorbed impurities during the sample preparations, samples were preheated at 50 °C for 30 minutes before collecting the TGA data. The nitrogen flow rates
for the balance compartment and the sample compartment were 40 mL/min and 60 mL/min, respectively. The temperature ramp rate was 2 °C/min from room temperature to 400 °C. The synthesized Na$_2$S was annealed and cleaned at 300 °C for 10 hours under Ar gas flow to get rid of any solvent absorbed on the powder surface. For comparison, pure Na$_2$S was obtained by annealing the commercial Na$_2$S •9H$_2$O at 300 °C for 10 hours under Ar gas flow.

In addition, hydrogen nuclear magnetic resonance spectroscopy (¹H NMR, JEOL ECA-500) was employed to determine the speciation of EtOH in the reaction solutions, by measuring the respective liquid phases at three stages: the initial EtOH/DME mixture, after adding the alkali metal but before the M$_2$S synthesis, and after the M$_2$S synthesis. The NMR samples were prepared by mixing 0.3 mL of sample solutions with 0.2 mL of benzene-D$_6$ and then loaded into quartz tube.

5.5.4 **Hydrogen Quantification:**

The concept of recovering H$_2$ from the proposed chemistry was examined by using QMS to quantify the H$_2$ produced from the reaction of alkali metal with alcohol. First, the QMS was calibrated by measuring a series of standard H$_2$/Ar mixtures, in which the H$_2$ flowrate was varied and the Ar flow rate was kept constant at 40 sccm (Figure 5.8A on page 78). Then, 30.0 mg of Na and 35 mL of DME were first loaded into the Parr reactor. After closing the reactor, a mixture of 5 mL of DME and 0.63 mL of EtOH was injected into the reactor, and the solution was stirred for several hours. Last, the gas in the headspace of the reactor was flushed out by flowing Ar through the reactor at the rate of 40 sccm and sent to QMS for the composition analysis. The instantaneous H$_2$ flow rate exiting the Parr reactor was obtained by multiplying the slope of the calibration curve and the experimental QMS intensity ratio of H$_2$ to Ar (Figure 5.8B). The total amount of H$_2$ produced was calculated by integrating the H$_2$ flow rate.

5.6 **Results and Discussion**

5.6.1 **The Model Reaction – Synthesis of Na$_2$S Nanocrystals**

The synthesis of M$_2$S-NCs via the EtONa-EtOH/DME solution was used as the model system to demonstrate the chemistry outlined in Figure 5.2 (page 67). The reaction setup is schematically illustrated in Figure 5.2A. Figure 5.2B plots the temporal online QMS signal intensities of Ar (black) and H$_2$S (red) collected from the reactor effluent. Initially, the 10 atom% H$_2$S/Ar mixture was directed through a bypass line to establish a baseline reading. When the bypass was closed at t = 285 s, both the Ar and H$_2$S fell exponentially with a time constant characteristic of the gas dynamics of the sampling apparatus. At t = 377 s, the inlet and outlet valves of the reactor were opened simultaneously; and the Ar signal immediately returned to its original value. In contrast, the H$_2$S signal continued to decay, and eventually dropped below the detection limit of the instrument. This indicates that at a minimum >99.9% of the H$_2$S supplied was consumed. The mass spectrum obtained during the bypass mode (Figure 5.2C, black) clearly shows the expected fragments of H$_2$S across mass/charge (m/z) ratios of 32–34. On the contrary, the spectrum taken
from the reaction effluent (Figure 5.2C, red) indicates no \( \text{H}_2\text{S} \); and the signal at \( m/z = 31 \) demonstrates that ethanol is regenerated during the reaction. The absence of \( \text{H}_2\text{S} \) in the effluent demonstrates that the reaction is spontaneous and proceeds to completion very rapidly at ambient temperature and pressure. The production rate is thus dependent on the \( \text{H}_2\text{S} \) flowing rate.

The phase purity and morphology of the solid product were studied by XRD, SEM, and EDX. The XRD pattern in Figure 5.2D (red) matches that of the \( \text{Na}_2\text{S} \) standard (black), indicating the production of anhydrous, phase-pure, and crystalline \( \text{Na}_2\text{S} \). According to the Scherrer equation,\(^{47}\) which correlates crystalline domains with peak width, \( \text{Na}_2\text{S} \) crystals are \( \sim 30 \) nm in size. The SEM images (Figure 5.2E) show that \( \text{Na}_2\text{S-NCs} \) aggregate as cubic particles of about \( 100 \) nm. In the EDX spectrum (Figure 5.2E, the inset), the atomic ratio of \( \text{Na} \) to \( \text{S} \) is 1.95, which agrees well with the theoretical value of 2 and indicates the high purity of the obtained \( \text{Na}_2\text{S-NCs} \). The \( \text{O} \) peak is ascribed to the air oxidation during the sample preparation; and the \( \text{C} \) signal is from the carbon tape used to immobilize the sample powder on the aluminum stub.

![Figure 5.2](image)

Figure 5.2 Proof of the concept via the synthesis of \( \text{Na}_2\text{S-NCs}. \) (A) Schematic diagram of the reaction setup; (B) Time evolution of the QMS signals of Ar (black) and \( \text{H}_2\text{S} \) (red) in the gas phase; (C) Mass spectra in the \( m/z \) window of 30 – 35 for the gaseous effluents through the bypass (black) and through the reactor (red); (D) XRD pattern of the obtained solid product (red) with the standard \( \text{Na}_2\text{S} \) pattern (black, JCPDS 00-023-0441); (E) SEM images of the obtained solid product, with a higher magnification as the inset; (F) EDX spectrum of the obtained solid product, together with the atomic percentages of elements therein.

The thermal stability of the product was analyzed with TGA (Figure 5.3 on page 68). The synthesized \( \text{Na}_2\text{S} \) was treated at \( 300 \) °C for 10 hours under Ar to remove the possibly adsorbed organic
solvent and then denoted as s-Na$_2$S. Commercial Na$_2$S·9H$_2$O (c-Na$_2$S·9H$_2$O) was treated in the same manner to produce a pure Na$_2$S reference and then denoted as c-Na$_2$S. For Na$_2$S·9H$_2$O (Figure 5.3A, black line), the abrupt weight loss of ~64% below 200 °C agrees well with the mass percent of H$_2$O in Na$_2$S·9H$_2$O (67.5%), indicating the complete dehydration. To get pure Na$_2$S from Na$_2$S·9H$_2$O, annealing at 300 °C for 10 hours under Ar was employed, as confirmed by XRD shown in Figure 5.3B, where the corresponding pattern from s-Na$_2$S is shown as comparison. The TGA results show that s-Na$_2$S (Figure 5.3A, red line) has comparable purity to c-Na$_2$S (Figure 5.3A, blue line), as indicated by their normally identical weight loss profiles.

![Figure 5.3](image)

Figure 5.3 (A) TGA results for commercial Na$_2$S·9H$_2$O (black) and two annealed Na$_2$S samples (red for s-Na$_2$S and blue for c-Na$_2$S); (B) XRD patterns of the annealed Na$_2$S powders (red for s-Na$_2$S and blue for c-Na$_2$S), with the Na$_2$S standard pattern (black, JCPDS 00-023-0441).

### 5.6.2 H$_2$ Quantification

The H$_2$ recovery and separation is easy, as the reaction of Na with EtOH (Reaction 5.3) is decoupled from the H$_2$S consumption (Reaction 5.2) and in both steps different chemicals exist in different phases. Figure 5.4A (page 69) is a representative mass spectrum of the headspace gas collected from the reactor after Reaction 5.3. H$_2$ is the predominant species detected along with the Ar carrier gas as well as signatures from the volatile ethanol and DME. Figure 5.4B illustrates the integrated volume of H$_2$ collected, which is in good agreement with the theoretical value based on the mole amount of Na supplied. The inset of Figure 5.4B shows the flowrate of H$_2$, which is calculated from the calibration line (Figure 5.8A) and the experimental QMS intensity ratio of H$_2$ to Ar (Figure 5.8B). The H$_2$ recovery yield is as high as 98%, demonstrating the stoichiometric completion of Reaction 5.3.
5.6.3 Speciation and Reuse of the Auxiliary Reagents

After Reaction 5.2, the supernatant was collected and analyzed using $^1$H NMR to confirm the complete transformation from EtONa to EtOH (Figure 5.5C on page 70). For comparison, the solutions of EtOH/DME before (Figure 5.5A) and after reaction with Na (denoted as NaOEt-EtOH/DME, Figure 5.5B) were also characterized. For all three solutions the detected peaks are from DME (two sets of peaks centered at ~3.22 ppm and ~3.40 ppm for the groups of -CH$_3$ and -CH$_2$-, respectively), benzene (the NMR solvent, singlet centered at ~7.25 ppm) and EtOH (three groups of peaks including a triplet, a singlet, and a quartet for CH$_3$-, -OH and -CH$_2$-, respectively). As the peak intensity of the solvent DME is very high, a break on the vertical axis is introduced between 2 and 50.

Comparison of Figures 5.5A, 5.5B and 5.5C shows that the chemical shifts of DME are not affected by the reactions due to its solvent identity and that the most prominent changes are the chemical shifts of -CH$_3$ and -CH$_2$- groups in EtO-. Before adding Na, pure EtOH in DME shows a triplet centered at ~1.158 ppm for -CH$_3$ and a quartet centered at ~3.600 ppm for -CH$_2$-. In contrast, for the EtONa-EtOH/DME solution, higher chemical shifts at ~1.199 ppm for -CH$_3$ and ~3.671 ppm for -CH$_2$- are observed. In addition, an exotic singlet at ~5.34 ppm emerges, probably due to NaOH formed from the hydrolysis of NaOEt because of air exposure during the NMR sample preparation and test. After the reaction of EtONa-EtOH/DME with H$_2$S, the NMR peaks for -CH$_3$ and -CH$_2$- groups shift back to the same positions as in EtOH/DME; additionally, there is no peak at ~5.34 ppm. The strong peak at ~1.15 ppm in all three cases is from -OH in the excess EtOH. These results qualitatively support the complete consumption of EtONa and the full recovery of EtOH.
With the full recovery of EtOH, the reaction supernatant was recycled to react with Na to regenerate EtONa for the next round of Na₂S nanocrystal synthesis. The corresponding time evolution of QMS (Figure 5.5D) and mass spectrum (Figure 5.5E) are identical to the 1st round using fresh EtOH and DME, indicating the complete capture of H₂S. The XRD results confirm the production of phase pure Na₂S-NCs (Figure 5.5F), validating the potential of recycling the auxiliary reagents. The crystal size according to the Scherrer equation is ~40 nm, slightly larger than that of the first-round-produced Na₂S-NCs. This may be ascribed to a faster crystal-growth rate due to the higher concentration of EtONa, which results from a small amount of loss of DME during the first round of reaction and sample purification.

5.6.4 Synthesis of Li₂S-NCs

Our synthesis strategy was also examined to produce Li₂S-NCs. The use of EtOLi-EtOH/DME encountered challenges. Although the H₂S abatement is fast and complete (Figure 5.9A and Figure 5.9B on page 79) as in the case of EtONa-EtOH/DME, the XRD pattern of the solid product (Figure 5.9C, red) matches with that of EtOLi (blue) rather than that of Li₂S (black). It is puzzling why Li₂S cannot be obtained and in what form the captured H₂S exists. Nevertheless, a noteworthy observation was that the addition of DME into the premade EtOLi-EtOH solution...
resulted in serious precipitation while no changes occurred upon the addition of DME for the EtONa system. We suspect that the resulting nanosheet crystals (Figure 5.9D) are an EtOLi-based complex that involves both DME and H₂S. Hence, subsequently, we searched for appropriate solvents by testing different chemicals.

Five solvents in total were tested (Figure 5.6 on page 72). Dioxane and 2-MeTHF displayed similar behaviors as DME, that is, the solutions of LiOEt-EtOH/2-MeTHF and LiOEt-EtOH/dioxane were cloudy; H₂S was consumed completely and instantly; but the XRD patterns of their solid products agree well with that of EtOLi (Figure 5.10 on page 79). After these initial setbacks, it was found that DBE, toluene and hexane yielded in the synthesis of phase pure Li₂S-NCs. All three solutions reacted with H₂S instantly and completely at room temperature. In Figure 5.6A, 5.6C, and 5.6E the XRD patterns of the pristine solid products (red) coincide with that of the Li₂S standard (black). The crystalline sizes extracted using the Scherrer equation are 12, 14, and 19 nm for DBE, toluene and hexane, respectively. SEM images show that the produced Li₂S-NCs using these three solvents exist in different morphologies: flake-shaped particles of ~50 nm in thickness for DBE (Figure 5.6B), spike-shaped particles of ~300 nm in width for toluene (Figure 5.6D), and irregular shaped particles of ~100 nm for hexane (Figure 5.6F). As the experimental conditions for Na₂S and Li₂S synthesis are controlled the same, the different results herein indicate that the choice of solvent is critical for the morphology control and that sodium ethoxide and lithium ethoxide have different reaction kinetics, whereas the exact reasons require more extensive studies and are beyond the scope of this paper.

After producing Li₂S-NCs with different morphologies by using different solvents, we continued to study different alcohols. A suitable alcohol should meet two requirements: A) It can react with the alkali metal efficiently to form the alkoxide and release H₂ (Reaction 5.3); and B) The solubility of M₂S in it is low to ensure a high production yield of M₂S as solid precipitates (Reaction 5.2). We studied straight chain alcohols ranging from ethanol to octanol. Both reactivity and M₂S solubility decrease with increasing the carbon chain length (Table 5.2 on page 80). Although M₂S is barely soluble in hexanol and octanol, their low reactivity makes their use too time-consuming. In contrast, both Li₂S and Na₂S exhibit some solubility in ethanol and butanol,⁵¹ but this does not significantly impact yield if the use of alcohol is limited to the amount required to form the alkoxide precursor.
5.6.5 Morphology Control of Na$_2$S-NCs

In contrast to the lithium system, the alcohol-mediated synthesis was much more robust for sodium, with controllable morphology of Na$_2$S-NCs by tuning the identities of the alcohol (ethanol or butanol) and the solvent (DME, 2-MeTHF, and dioxane), as shown in Figure 5.7 (page 73). All the reactions proceed to completion very rapidly at ambient temperature and pressure. For the ease of comparison, a second SEM image of Na$_2$S obtained from using ethanol and DME is shown in Figure 5.7A. Changing the solvent to 2-MeTHF (Figure 5.7B) and dioxane (Figure 5.7C) produced spherical secondary clusters (SCs), which are self-assembled from primary particles. The size of SCs is about several micrometers and the primary particles are ~200 nm. SCs hold the potential to integrate the advantages of both bulk materials (high energy density) and NCs (high specific energy and cycling stability) for advanced rechargeable batteries. In addition, they are also promising materials for making solid electrolytes. As for the butanol series, all solvent systems (Figure 5.7D-F) produced well-dispersed Na$_2$S-NCs of ~200 nm with no generation of SCs. Figure 5.11 (page 80) shows the XRD patterns of all Na$_2$S products from the above six reactions. The crystalline sizes calculated according to Scherrer equation for all the produced Na$_2$S are all ~30 nm. Thus, the substantial difference in morphologies of the final Na$_2$S products shown in Figure 5.7 primarily reflects the different propensity of primary crystals to aggregate.

The aggregation propensity is mainly governed by the interactions between NCs and solvent molecules. We speculate that the surfaces of Na$_2$S-NCs are covered with the alkoxide groups during
growth, which makes the particle surface slightly charged. Ethanol and butanol are expected to have similar capability to induce the surface change, since they have comparable acidity ($pK_a$), polarity, and dielectric constant, as shown in Table 5.1 (page 74). However, butoxide-passivated Na$_2$S-NCs would have a lower propensity to aggregate due to its longer carbon chain that can result in stronger hydrocarbon expulsions. As for the solvent molecules, those with higher polarities and dielectric constants can stabilize the surface charges of Na$_2$S-NCs more effectively, further decreasing the aggregation possibility. This interpretation is supported by the trends of polarity and dielectric constant for these three solvents, DME > 2-MeTHF > Dioxane (Table 5.1). In addition, it has also been reported that colloidal NCs usually do not tend to self-assemble or aggregate in polar organic solvents due to weak interparticle electrostatic interactions. The sodium system was not immune to challenges. Interestingly the solvents that were shown to be successful for Li$_2$S, namely DBE, toluene and hexane, were problematic, producing mixtures of Na$_2$S and NaHS, as shown by the XRD data in Figure 5.12 (page 80). Further work is underway to better understand the complex chemistry among metal, solvent and reagent.

Figure 5.7 Na$_2$S morphology tuning by changing alcohols and solvents. SEM images of the obtained solid products from the reactions of H$_2$S with sodium ethoxide (A-C) or sodium butoxide (D-F) in the solvents of DME (A and D), 2-MeTHF (B and E) or dioxane (C and F).
<table>
<thead>
<tr>
<th>Properties</th>
<th>Molecular Structure</th>
<th>Relative Polarity$^{55}$</th>
<th>Dielectric Constant (25 °C)</th>
<th>$p_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td>![DME structure]</td>
<td>0.231</td>
<td>7.2</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>![Dioxane structure]</td>
<td>0.164</td>
<td>2.25</td>
<td>-</td>
</tr>
<tr>
<td>2-MeTHF</td>
<td>![2-MeTHF structure]</td>
<td>~ 0.207$^{a}$</td>
<td>6.97</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol</td>
<td>![Ethanol structure]</td>
<td>0.654</td>
<td>25</td>
<td>15.5$^{33}$</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>![1-Butanol structure]</td>
<td>0.586</td>
<td>18</td>
<td>16.10$^{56}$</td>
</tr>
</tbody>
</table>

a. The relative polarity of 2-MeTHF is considered close to that of THF (0.207).

### 5.7 Conclusion

In conclusion, we have demonstrated a simple and scalable method to synthesize anhydrous sodium sulfide (Na$_2$S) and lithium sulfide (Li$_2$S) nanocrystals (NCs) through reactive precipitation using alkali metal alkoxide (ROM) and hydrogen sulfide (H$_2$S) as reagents in organic solutions. M$_2$S-NCs are critical for the development of both cathodes and solid-state electrolytes for next generation rechargeable batteries. H$_2$S abatement is complete, with the hydrogen in H$_2$S being stored in the alcohol byproduct. The alcohol can be recycled to react with new M to replenish ROM for the subsequent rounds of synthesis, recovering the hydrogen in the form of H$_2$. Both steps are thermodynamically favorable, proceeding spontaneously, rapidly, completely, and irreversibly at ambient temperature and pressure. The net consequence is H$_2$S + 2M $\rightarrow$ M$_2$S + H$_2$, transforming a hazardous waste into two valuable chemicals. The transformations to both M$_2$S-NCs and H$_2$ require no energy and proceed with high atom economy, purity, and easy separation. By tuning the alcohol and solvent, M$_2$S-NCs of different morphologies can be produced. These results clearly manifest that this green-inspired approach is potentially transformative for scalable manufacturing of M$_2$S-NCs. Work is ongoing to better understand the nucleation/growth kinetics and to evaluate these materials in battery applications.

### 5.8 References


5.9 Supporting Information

Figure 5.8 (A) H₂ calibration curve of H₂ flowrate versus QMS intensity ratio of H₂/Ar (AMU2/AMU40); (B) Real time QMS intensity ratio of H₂/Ar in the reactor.
Figure 5.9 Characterizations for the reaction of H$_2$S with EtOLi-EtOH/DME. (A) Time evolution of QMS for Ar (black) and H$_2$S (red); (B) Mass spectra in the m/z window of 30 – 35 for the gaseous effluents through the bypass (black) and the reactor (red); (C) XRD patterns of the obtained solid product (red) from the reaction and synthesized EtOLi powder (blue) with the standard pattern of Li$_2$S (black, JCPDS: 04-003-6927); (D) SEM images of the obtained solid products.

Figure 5.10 XRD results of the produced solid powders from the reactions of H$_2$S with EtOLi in 2-MeTHF (A) and dioxane (B).
Table 5.2 The solubility of \( \text{Na}_2\text{S} \) and \( \text{Li}_2\text{S} \) in alcohols.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \text{Na}_2\text{S} )</th>
<th></th>
<th>( \text{Li}_2\text{S} )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (g/100g of solvent)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>8.47</td>
<td>3.99</td>
<td>5.99</td>
<td>1.82</td>
</tr>
<tr>
<td>1-butanol</td>
<td>1.43</td>
<td>0.83</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>0.83</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>1-octanol</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Figure 5.11 XRD results of the synthesized \( \text{Na}_2\text{S} \) from the reactions of \( \text{H}_2\text{S} \) with \( \text{EtONa} \) (A-C) and \( \text{BuONa} \) (D-F) in the solvents of DME (A and D), 2-MeTHF (B and E) or dioxane (C and F).

Figure 5.12 XRD results of the solid products from the reactions of \( \text{H}_2\text{S} \) with \( \text{EtONa} \) in DBE (A), toluene (B) and hexane (C).
CHAPTER 6
STUDY OF LITHIUM SILICIDE NANOPARTICLES AS ANODE
MATERIALS FOR ADVANCED LITHIUM ION BATTERIES

6.1 Abstract

The development of high-performance silicon (Si) anodes for next generation of lithium ion batteries (LIBs) evokes increasing interest in studying its lithiated counterpart – lithium silicide (Li\textsubscript{x}Si). This article reports a systematic study of three thermodynamically-stable phases of Li\textsubscript{x}Si (x = 4.4, 3.75, and 2.33) plus nitride-protected Li\textsubscript{4.4}Si, which are synthesized via the high-energy ball milling technique. All three Li\textsubscript{x}Si phases show improved performance over unmodified Si, where Li\textsubscript{4.4}Si demonstrates optimum performance with discharging capacity of 3306 mAh/g initially and maintains above 2100 mAh/g for over 30 cycles and above 1200 mAh/g for over 60 cycles at the current density of 358 mA/g-Si. A fundamental question studied is to understand if different electrochemical paradigms, that is, delithiation first or lithiation first, influence the electrode performance. No significant difference in electrode performance is observed. When a nitride layer (Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}) is created on the surface of Li\textsubscript{4.4}Si, the cyclability is improved to retain the capacity above 1200 mAh/g for more than 80 cycles. By increasing the nitridation extent, the capacity retention is improved significantly from the average decrease of 1.06% per cycle to 0.15% per cycle, while the initial discharge capacity decreases due to the inactivity of Si in the Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z} layer. Moreover, the Coulombic efficiencies of all Li\textsubscript{x}Si-based electrodes in the first cycle are significantly higher than that of Si electrode (~ 90% vs. 40 - 70%).

6.2 Keywords

lithium silicide, lithium ion batteries, anode, nanoparticles, nitridation

6.3 Introduction

The increasing demands for more advanced consumer electronics, electric vehicles, and stationary facilities call for next generation of rechargeable batteries with higher specific energy (energy per mass) and energy density (energy per volume) than the current generation of lithium ion batteries (LIBs),\textsuperscript{1,2} which largely use lithium metal oxide (LMO) cathodes and graphite anodes. Among all candidates scrutinized for the anode, silicon (Si) is one of the most promising materials, due to its charge capacity being up to ten times higher than that of graphite.\textsuperscript{3} However, Si suffers from volume fluctuation-induced poor cycling stability (cyclability).\textsuperscript{4,5} The volume fluctuation,\textsuperscript{3,6} that is, repeated volume expansion (the lithiation process) and volume contraction (the delithiation process) during the discharging/charging cycles, causes two serious issues: 1) damage of the electrical contact between Si and the current collector; 2) recurrent growth/destruction of a shielding layer – the solid electrolyte interphase (SEI) – on the electrode surface.\textsuperscript{8}
Thus, enormous efforts have been invested to construct stable Si electrodes.\textsuperscript{4-6,9-23}

Arguably, an ideal concept is to encapsulate every Si nanoparticle (NP) inside a conductive and robust shell with preset void space contiguous to the Si core (or yolk), i.e., to produce a core@void@shell structure.\textsuperscript{10-16} This void-space-engineering strategy allows volume fluctuation to occur only inside the shell. Consequently, stable electrical contact and SEI layer are maintained, resulting in improved cyclability.\textsuperscript{10-15} In studies to date, the Si cores are either nanospheres or nanowires;\textsuperscript{10-13} the shell materials include amorphous carbon from pyrolyzing organic compounds,\textsuperscript{10,11} crumpled graphene sheets,\textsuperscript{15} conductive polymers,\textsuperscript{17,18} and SiO$_2$/C composite.\textsuperscript{12} Two alternatives of the core@void@shell structure are hollow Si nanostructures\textsuperscript{14,19-21} and pomegranate-shaped Si secondary clusters (entities of assembled NPs).\textsuperscript{22,23} Although the electrode performance in all these systems has been significantly enhanced, several challenges remain unresolved.

First, the Coulombic efficiency (CE) of Si in the first cycle is low (typically 50 - 80\%),\textsuperscript{24,25} because the SEI layer formation consumes a large amount of lithium.\textsuperscript{26} This causes difficulties in matching the capacity of anode/cathode pairs when assembling practical batteries. Second, some techniques are difficult to scale up for industrial applications such as the use of hydrogen fluoride (an extremely hazardous chemical) in presetting the void space.\textsuperscript{11,14,19-21} Third, at present there lacks a suitable existing cathode material to pair with Si for making advanced batteries. For instance, because of the limited charge capacity of LMO (\textasciitilde 160 mAh/g), a full battery assembled from Si anode and LMO cathode will not store appreciably more energy than an existing LIB made from graphite anode and LMO cathode.\textsuperscript{27} The extensively-studied sulfur (S) cathode can store much more charge (1676 mAh/g-S), but making a full battery with it requires a lithium-containing anode, for which Si is not eligible.

The first challenge has been attempted by adding a pre-lithiation reagent during electrode fabrication\textsuperscript{26,28} or pre-lithiating the Si electrode before battery assembly.\textsuperscript{29,34} Mitigation of the second challenge requires further improvements or innovation in electrode fabrication. The solution to the third challenge is to develop lithium silicide (Li$_x$Si) anodes, which can not only be paired with S-cathodes but also hold the potential to overcome the other two challenges.\textsuperscript{35,36} Since Li$_x$Si is lithiated silicon, it can function as both the electrode and the pre-lithiation reagent. In principle, void space can be created around each Li$_x$Si particle after extracting Li$_x$ during the initial delithiation process to effectively accommodate the subsequent lithiation process. The volume of the void space created is dependent on the lithium content in Li$_x$Si, where an optimal value of x is expected. Further, if a conductive and robust shell can be conformally coated outside each particle, the Li$_x$Si anode can enjoy all benefits that the typical void-space-engineering strategy has achieved for the Si anode. In addition, by eliminating the need of presetting the void space, the Li$_x$Si anode can be fabricated without using hazardous hydrogen fluoride. It is noted that, due to the high reactivity of Li$_x$Si, an inert atmosphere is required for handling Li$_x$Si and synthesis of the desired
A conductive and robust shell is challenging.\textsuperscript{26, 33, 37} Nevertheless, with such attractive features, Li\textsubscript{1-x}Si electrodes deserve a systematic exploration to better understand their promise and challenges.

Compared with Si, the existing studies on Li\textsubscript{1-x}Si are very limited. In these reports, the Li\textsubscript{1-x}Si electrodes are primarily amorphous Li\textsubscript{1-x}Si, limited by the synthetic methods such as the electrochemical lithiation of Si in a temporary battery,\textsuperscript{30, 31} and chemical lithiation by putting Si in contact with lithium metal or lithium compounds.\textsuperscript{28, 31, 32} There are a couple of methods to make Li\textsubscript{1-x}Si crystals.\textsuperscript{27, 36-38} The first method is thermochemical synthesis by reacting Li metal with Si powder at elevated temperatures.\textsuperscript{27} The second method is mechanochemical synthesis by milling Li metal and Si powder in a ball mixing apparatus.\textsuperscript{36, 39} However, the performance achieved so far on crystalline Li\textsubscript{1-x}Si is poor; there are no systematic studies on different Li\textsubscript{1-x}Si phases; and surface protection is still a scarcely-attempted topic.\textsuperscript{26, 33}

Due to the high reactivity of Li\textsubscript{1-x}Si,\textsuperscript{37} surface protection will be imperative before building the conductive and robust shell for accommodating the volume fluctuation. Learning from the fact that Li can readily react with nitrogen (N\textsubscript{2}) gas at room temperature to form lithium nitride (Li\textsubscript{3}N),\textsuperscript{40, 41} we hypothesize that Li\textsubscript{4.4}Si NP can also react with N\textsubscript{2} to generate a nitride-like layer outside its surface. Li\textsubscript{3}N is thermally robust, with a high melting point of 810 °C.\textsuperscript{42} It is chemically stable in many organic solvents, such as dimethylformamide (DMF).\textsuperscript{43} It is mechanically strong with a high Young’s modulus of 150 GPa,\textsuperscript{42} which is comparable with that of carbon fibers (170 GPa).\textsuperscript{44} Particularly, it is also a superionic Li-ion conductor with an exceptional conductivity of 0.1 S/m,\textsuperscript{40, 45} ten times better than most solid state electrolytes and comparable with many organic liquid electrolytes.\textsuperscript{46} Due to these remarkable properties, Li\textsubscript{3}N has been increasingly used as surface protection for developing Li-metal anodes.\textsuperscript{41, 45} Because the diffusion coefficient of nitrogen atoms in silicon is as low as 3.66 × 10^{-15} \text{cm}^2\text{s}^{-1}, two orders magnitude lower than that of phosphorus,\textsuperscript{47} nitrogen atoms are expected not to enter the bulk. Due to the presence of Si, the nitride layer is expected not to exist as pure Li\textsubscript{3}N and better denoted as Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}. The nitridation may result in Li\textsubscript{x}Si-based electrode materials with improved cyclability and provide a promising surface-protection method for the subsequent fabrication of the conductive and robust shell.

We herein report a systematic study on three thermodynamically-stable phases of Li\textsubscript{x}Si (x = 4.4, 3.75, and 2.33) plus surface-nitridated Li\textsubscript{4.4}Si (Li\textsubscript{4.4}Si@Li\textsubscript{x}N,Si\textsubscript{y}), which are synthesized via high-energy ball milling. Their electrode performance is systematically assessed, and found to be superior to Si powder in terms of charge capacity, cyclability, and Coulombic efficiency.

\textbf{6.4 Experimental Section}

\textbf{6.4.1 Chemicals and Materials}

Lithium grains (Li, ACS reagent, stick dry), silicon powder (Si, 325 mesh 99%), and hexane (anhydrous, 95%) were purchased from Sigma-Aldrich. Lithium foil (Li, 99.9% trace metals basis, 0.75 mm thick × 19 mm wide) was purchased from Alfa Aesar. The electrolyte of 1.0 M lithium
hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/diethyl carbonate (DEC) (volume ratio of 1:1) was purchased from BASF. Acetylene black (AB, 35 - 45 nm), polyvinylidene fluoride (PVDF, - (C₂H₂F₂)n -, >99.5%), and copper foil (Cu, 99.99%, 9 µm) were purchased from MTI Corp. Copper foam (Cu, PPI = 70) was purchased from DeSiKe Inc., China. AB and PVDF were dried in a vacuum oven at 60 ºC for 24 hours before use. All other chemicals were used as received.

6.4.2 Synthesis of Electrode Materials

Si: In an argon-filled glove box (MBraun, LABstar), commercial Si micropowder and hexane (used as the lubricant) were loaded in a stainless-steel ball mill jar (35 mL) with two ½ inch balls inside and then mounted to a high energy ball mill (SPEX, Mixer/Mill 8000M) outside of the glove box to ball mill 300 mins.

LiₓSi: Three types of LiₓSi (x = 4.4, 3.75, and 2.33) were synthesized via the high energy ball milling method we published previously. Briefly, in the argon-filled glove box, appropriate amounts of Li grains, Si powder and hexane were loaded in the ball mill jar and mounted to a high-energy ball mill. The milling periods were 300 min for Li₄.₄Si and Li₂.₃₃Si, and 100 min for Li₃.₇₅Si. Last, LiₓSi products were collected after evaporating the hexane and stored dry for further use.

Li₄.₄Si@LiₓNₓSi₁₋: This group of materials was obtained via surface nitridation of premade Li₄.₄Si. Typically, inside an argon-filled glove box, 0.7665 g of Li₄.₄Si powder and one ball were loaded in a ball mill jar. Then, the jar was transferred into a nitrogen-filled glovebox (VAC Nexus) to fill the jar with N₂ gas. After that, the jar was mounted onto the mill for 20 minutes to achieve a sufficient reaction between Li₄.₄Si and N₂. Using one ball in this process was to assure the surface nitridation and minimize the mechanical damage to the Li₄.₄Si particles. The obtained materials were denoted as Li₄.₄Si@LiₓNₓSi₁-₁. Similarly, the samples after one or two more times of nitrogen treatments were denoted as Li₄.₄Si@LiₓNₓSi₁₋₂ and Li₄.₄Si@LiₓNₓSi₁₋₃, respectively. While in principle an alternative method of using less Li₄.₄Si and milling just once could be considered for the latter two samples, this was not feasible in our case because the amount of solid materials loaded in the jar must be above a threshold to minimize ball debris.

6.4.3 Characterizations

X-ray diffraction (XRD) measurements were conducted on a Philips X’Pert X-Ray diffractometer using Cu Kα radiation (λ = 0.15405 nm). The samples were prepared in an argon--filled glove box by adding solid products onto glass substrates. A drop of mineral oil was applied to cover the sample powder to prevent reactions with moisture and oxygen in the air during measurements. The background from mineral oil (a smooth and broad peak centered at 17.2° spanning from 10° to 25°) was subtracted and corrected prior to data processing. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) data were taken on a Field Emission SEM (JEOL JSM-7000F FESEM) with a JEOL EDAX Detector. The samples were prepared by immobilizing the obtained sample powder on an
aluminum stub using a double-sided carbon tape. The accelerating voltage was 5 kV and 20 kV for taking SEM images and EDS spectra, respectively. High-resolution transmission electron microscopy (HRTEM) and scanning TEM (STEM) images were acquired in bright field (BF) and high-angle annular dark field (HAADF) modes on an FEI Talos instrument, with ChemiSTEM detector for EDS analysis. Samples were prepared by brushing holey C grids with the dry powder and immediately loaded into the TEM to minimize air exposure.

6.4.4 Electrode Fabrication and Electrochemical Analysis

Copper (Cu) foam was cut into small discs of 10 mm in diameter using a compact precision disc cutter (MTI Corp., MSK-T-07). Then the small discs of Cu foam were cleaned by sonication in soap water for 30 minutes, nanopure water (18.3 MΩ cm⁻¹, obtained from a Barnstead water purification system) for 30 minutes, 0.5 M HCl aqueous solution for 10 minutes, and nanopure water for 10 minutes. After cleaning, the Cu foam discs were dried in a vacuum oven (MTI Corp., EQ-DZF-6020-FP) at room temperature for 24 hours. To fabricate electrodes the respective active material, AB, and PVDF (whose weight percentages are provided in the respective context) were first blended manually in a mortar or through ball milling for 20 minutes. Then around 1.2 mg of the mixture was dropped and spread onto Cu foam current collector. Pellet press (Parr Instrument Company) was used to assure the electrode materials attaching tightly on the Cu foam. After that, the Swagelok half-cell batteries were assembled by using the prepared electrode, Li foil counter electrode, polypropylene membrane (Celgard 2500) separator, and electrolyte of 1.0 M lithium hexafluorophosphate (LiPF₆) in EC/DEC. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EISs) were conducted on a potentiostat (Princeton Applied Research, Versastat 4), for which the applied alternating voltage was 10 mV in amplitude and 100 kHz to 0.01 Hz in frequency. The cycling stability was assessed via the galvanostatic technique with a potential window of 0.05 V - 1.0 V at 0.1 C (1C = 3580 mA/g-Si according to the theoretical value for amorphous Li₃.75Si, the most-lithiated phase at 0.05 V), by using an 8-channel battery analyzer (MTI Corp., BST8-MA).

6.5 Results and Discussion

6.5.1 Characterization of Si, Li₄.₄Si, and Li₄.₄Si@Li₃NₓSi₋₁

Figure 6.1 (page 86) shows the XRD (A - C) and SEM (D - F) characterizations of three electrode materials: Si, Li₄.₄Si, and Li₄.₄Si@Li₃NₓSi₋₁. The Si sample (Figure 6.1A and Figure 6.1D), which is prepared by ball-milling commercial Si micropowder (whose XRD and SEM data are shown in Figure 6.10 on page 100 for comparison), consist of both nanoparticles (<200 nm) and microparticles (>1 µm). The as-synthesized Li₄.₄Si (Figure 6.1B and Figure 6.1E) mainly consists of ~200 nm NPs with the crystalline sizes of 15 nm according to the Scherrer equation calculation. The XRD pattern of Li₄.₄Si@Li₃NₓSi₋₁ (Figure 6.1C) reveals that the crystalline phase therein is still Li₄.₄Si, without diffraction peaks that can be assigned to Li₃N. The peak width is slightly
broader than that of Li$_{4.4}$Si (Figure 6.1B), consistent with the corresponding smaller crystal sizes (12 nm). The SEM images in Figures 6.1E and 6.1F show that they have similar morphologies despite slightly different extents of aggregation. XRD peaks of Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (Figure 6.1C) shift slightly to higher angles by 0.2° vs. those of Li$_{4.4}$Si, as shown by the inset of Figure 6.1C to highlight the strongest peak at ~40°. Higher angles herein, which indicate smaller lattice constants, could result from two possibilities. First, a core@shell like structure is formed, as the lattice mismatch between the surface material and the core material can generate huge pressure to compress the core.$^{49-51}$ Second, a homogenous alloy is formed, if the newly-introduced element is smaller than the displaced element and diffuses through the entire host material (as described by the Vegard’s law).$^{52}$ However, considering the very small diffusion coefficient of nitrogen in silicon as mentioned above,$^{47}$ it does not seem feasible for the nitrogen atoms in our sample to migrate through the entire particle to form an alloy, negating the second possibility. The direct evidence for realizing the Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 is presented below.

Figure 6.1 XRD patterns (A - C) and SEM images (D - F) of three electrode materials: Si (A and D), Li$_{4.4}$Si (B and E), and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (C and F).

The initial indication of successful nitridation was observed during materials synthesis: 1) The ball-milling jar after each nitridation treatment was found to be under negative pressure, in stark contrast to the normal pressure when filling argon to synthesize Li$_{4.4}$Si; 2) The nitridated samples were less reactive than Li$_{4.4}$Si as evidenced by the much weaker bubbling (hydrogen evolution) when being treated with ethanol and the zero observation of pyrophoricity.$^{37}$ STEM and EDS characterizations of Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (Figures 6.2, 6.11-6.15, and Table 6.1) provide stronger evidence for the nitridation and formation of Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 structure. Figure
6.2B and Figure 6.2D (page 88) show that agglomerations of the Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ sample have distinct layers of lower contrast around the edges, as opposed to the untreated Li$_{4.4}$Si sample (Figure 6.2A and Figure 6.2C) that has similar morphology throughout its structure. According to statistical EDS analysis (Figure 6.11 and Table 6.1), these edge areas typically have higher percentages of nitrogen. EDS elemental mapping of Li$_{4.4}$Si (Figure 6.12 on page 102) shows that the contours of Si, N, and O are essentially identical to the HAADF contour. In contrast, the EDS elemental mapping of Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ (Figure 6.13 on page 103) shows that the Si contour is smaller than those of N, O and HAADF, indicating a N-rich surface. High resolution TEM imaging (Figure 6.2E and Figure 6.2F) and FFT analysis (Figure 6.14 on page 103) shows that the outer layer of Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ is amorphous – a direct consequence of surface nitridation. On average, EDS measurements (Figure 6.11 and Table 6.1) from the TEM show that the molar ratios of N/Si & N atomic percentages for Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ are 0.11 & 9.7 at.% and 0.26 & 20.8 at.%, respectively. These observations are consistent with the EDS measurements during SEM analysis (Figure 6.15 on page 103). Nitrogen content in the untreated sample Li$_{4.4}$Si is attributed to unavoidable air exposure during sample preparation, as the material is opened to atmosphere for a brief time before loading into the microscope. While we cannot rule out the contribution of air exposure to the detected nitrogen in the case of Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$, the observed enhanced chemical stability after nitridation implies that such possibility is low.

6.5.2 Electrode performance of Si, Li$_{4.4}$Si, and Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$

The cycling performance of electrodes prepared from 80 wt% of the active materials, 12 wt% of AB, and 8 wt% of PVDF is shown in Figure 6.3 (page 89). Figure 6.3A illustrates the specific capacity in both forms of charging capacity (solid symbols) and discharging capacity (open symbols). The Si electrode starts with discharging/charging capacity of only 1409/628 mAh/g and dies after 18 cycles, whereas the commercial Si starts at 3041/1875 mAh/g and dies after 14 cycles (black line in Figure 6.16 on page 104). By referring to similar reports in the literature, the inferior performance of the ball-milled Si to the untreated commercial Si is ascribed to the formation of amorphous silicon-iron alloy. While we acknowledge that Si anodes of remarkable performance have been demonstrated by many researchers through extensive optimizations of materials synthesis and electrode fabrication, the Si materials presented above are fair comparisons for our studies of Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ whose electrodes were prepared in the same way. The Li$_{4.4}$Si electrode shows significant improvement, with an initial discharging capacity of 2384 mAh/g and 1132 mAh/g at the 10th cycle. This performance compares favorably with other Li$_x$Si studies in the literature as shown in Table 6.2 (page 104). The Li$_{4.4}$Si@Li$_x$N$_y$Si$_{z-1}$ electrode performs the best, with initial discharging capacity of 2808 mAh/g and 1567 mAh/g at the 10th cycle. Its capacity is above 1200 mAh/g at the 50th cycle – double that of Li$_{4.4}$Si. The capacity retentions...
(Figure 6.3B), which are extracted from Figure 6.3A, present a clearer view on the cyclability of these three electrodes. For the first 20 cycles, the average discharging capacity degradations are 4.6% per cycle for Si, 3.0% per cycle for Li$_{4.4}$Si, and 2.6% per cycle for Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1, respectively. After that, the degradation per cycle is 1.0% for Li$_{4.4}$Si and 0.58% for Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1. Furthermore, the Coulombic efficiencies for Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 are significantly superior to that of Si (Figure 6.3C), that is, 79.8% and 89.2% vs. 43.2%.

![Figure 6.2](image_url)

Figure 6.2 S/TEM of Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 samples: High-angle annular dark field (HAADF) STEM imaging (A and B), bright-field STEM imaging (C and D), and bright-field TEM imaging (E and F). Scale bars in A – D are all 500 nm and scale bars in E – F are both 20 nm.
Figure 6.3 Plots of specific capacity (A), capacity retention (B), and Coulombic efficiency (C) against the cycle number for three electrodes made from Si (black), Li\textsubscript{4.4}Si (blue), and Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} (red). The charging capacity (solid symbols) and the discharging capacity (open symbols) are calculated versus the mass of silicon and measured with the galvanostatic current of 358 mA/g-Si (0.1 C, 1C = 3580 mA/g-Si).

6.5.3 The Effect of Nitridation Extent

After confirming the advantage of surface nitridation, we studied the effect of nitridation extent by repeating the nitridation process one and two more times to synthesize two additional samples, which are denoted as Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} and Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z}, respectively. Similar to Li\textsubscript{4.4}Si, the XRD peaks of these Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} samples (Figure 6.4A and Figure 6.4B on page 90) also shift to higher angles compared with those of Li\textsubscript{4.4}Si. The comparable magnitudes of peak-position shift for Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} and Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} may be ascribed to comparable thicknesses of the nitride layer; a larger shift in Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} implies a thicker nitride shell.\textsuperscript{49-51} The comparable and broader peak widths in the latter two cases (full width at half maximum of 0.91° vs. 0.66°) indicate smaller crystal sizes due to the extended nitridation. The cycling performance of these three materials (Figure 6.4C and Figure 6.4D) show improved cycling stability with increasing the nitridation extent. For Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z}, the first discharging capacity is 1542 mAh/g with an average degradation rate of 2% per cycle for the first 20 cycles and 0.71% per cycle for the subsequent cycles. For Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z}, the first discharging capacity is 745 mAh/g with an average degradation rate of 0.33% per cycle for the first 60 cycles and 0.15% per cycle subsequently until the 300\textsuperscript{th} cycle (Figure 6.17 on page 105). The tradeoff of realizing their improved cyclability compared with Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} is their lowered capacity. The initial delithiation capacity for Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} is 2610 mAh/g, 87% of the initial delithiation capacity of Li\textsubscript{4.4}Si. For Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} and Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z}, the values are 1404 mAh/g (47%) and 723 mAh/g (24%), respectively. EDS analysis (Figure 6.15C on page 103 and Figure 6.18 on page 105) shows that the molar ratios of N/Si in three Li\textsubscript{4.4}Si@Li\textsubscript{i},N\textsubscript{i}Si\textsubscript{z} materials are 0.27, 0.62, and 1.24, respectively, corresponding to ~90% of nitrogen reaction yield that falls in the expected range. From these values, we can further calculate the fractions of unreacted Li\textsubscript{4.4}Si to be 84%, 58%, and 15%, respectively. The qualitative agreement between the achievable capacity and the percentage of the unreacted Li\textsubscript{4.4}Si imply that the intact Li\textsubscript{4.4}Si is the only (primary) contributor to the capacity. Overall, these results indicate that the nitridation protection can improve the
electrode performance and may enable the subsequent fabrication of more conductive and robust shells to develop stable Li$_x$Si electrodes of high performance.

Figure 6.4 Investigation of the nitridation effect. (A) XRD patterns of Li$_{4.4}$Si (black), Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (red), Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-2 (blue), Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-3 (magenta), and commercial Li$_3$N (green). (B) The region of 38° - 48° in (A) to highlight the position shift of the strongest diffraction peak. (C) Plots of the specific capacity in the charging capacity (solid symbols) and the discharging capacity (open symbols) against the cycle number for three different Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$ samples. (D) The corresponding plots of capacity retention with respect to (C).

6.5.4 The Effect of Electrode-Fabrication Procedure

Next, we studied the effect of electrode-fabrication procedure by making two changes: i) ball milling the electrode components instead of the previous manual mixing, and ii) increasing the percentage of AB. The first change was expected to improve the homogeneity and interconnections among the active material, AB, and PVDF; the second change was expected to improve the electrode conductivity and volume accommodation. Compared with the original procedure of manually mixing 80 wt% of the active material, 12 wt% of AB and 8 wt% of PVDF (Figure 6.3 and Figure 6.4), the second procedure was to ball mill the same electrode-components for 20 minutes
and the third procedure was to change the electrode components to 64 wt% of the active material, 28 wt% of AB and 8 wt% of PVDF, with other operations the same as in the second type. For Li<sub>4.4</sub>Si and Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1, the third type shows the best performance, whereas there is no appreciable improvement for Si (Figure 6.5). Note that the third electrode-fabrication procedure is applied for all studies below. Again, the performances of three active materials follow the same trend of Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1 > Li<sub>4.4</sub>Si > Si. While Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1 outperforms Li<sub>4.4</sub>Si in the specific capacity only after the 60<sup>th</sup> cycles (Figure 6.5A), its capacity retention is superior starting from the first cycle (Figure 6.5B). The Coulombic efficiencies of Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1 and Li<sub>4.4</sub>Si are improved up to 92 – 99% (Figure 6.5C). The comparison of three different electrode-fabrication procedures in the same figure (Figure 6.19 on page 106) confirms that ball-milling and a relatively-higher AB percentage are beneficial, being consistent with our expectations and similar reports in the literature. The ball-milling treatment that can improve homogeneity and interconnection seems to play the major role in the performance enhancement.

![Figure 6.5 Plots of specific capacity (A), capacity retention (B), and Coulombic efficiency (C) against the cycle number to compare the performance of Si, Li<sub>4.4</sub>Si and Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1 electrodes prepared by ball milling the mixture of 64% active materials, 28% AB and 8% PVDF.](image)

Afterward, we investigated the lithiation-and-delithiation mechanisms of Li<sub>4.4</sub>Si and Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1 with Si as comparison (Figure 6.6 on page 92 and Figure 6.20 on page 106). Figures 6.6A-C show their charging/discharging profiles. In the case of Si, a sloping plateau at ~0.67 V due to the SEI formation in the 1<sup>st</sup> discharging profile disappears in the subsequent cycles (Figure 6.6A). Two other sloping plateaus at ~0.23 V and ~0.10 V result from the progressive lithiation of Si. As Li<sub>4.4</sub>Si and Li<sub>4.4</sub>Si@Li<sub>i</sub>N<sub>y</sub>Si<sub>z</sub>-1 are in the lithium-rich states, the initial treatments were to delithiate Li<sub>4.4</sub>Si, showing a plateau at ~0.4 V (Figure 6.6B and Figure 6.6C). In the subsequent cycles, the similar voltage profiles for all three electrodes indicate that they follow the same charging/discharging mechanism, as expected. This conclusion is further corroborated by the dQ/dV plots (Figure 6.21 on page 107) that are derived from the charging/discharging profiles. All three materials show the essentially comparable features with two
lithiation peaks (~0.07 V and ~0.22 V) and two delithiation peaks (~0.30 V and ~0.49 V), which indicate phase-transition reactions as reported in the literature.\textsuperscript{27}

Figures 6.6D-F show three cycles of cyclic voltammograms (CVs) for these three materials. The cathodic peak (lithiation) at 0.59 V in the 1\textsuperscript{st} half cycle of Si (Figure 6.6D) results from the SEI formation, coinciding with the plateau observed at 0.7 V in Figure 6.6A.\textsuperscript{56-59} In the subsequent delithiation processes, the main anodic peak at 0.59 V indicate the delithiation through phase-transition.\textsuperscript{58} Starting from the 2\textsuperscript{nd} cycle only one cathodic peak at 0.15 V is observed, indicating the conversion of crystalline Si to Li\textsubscript{4.4}Si.\textsuperscript{58} The slight increase of peak intensities with cycling is ascribed to improved electrolyte accessibility.\textsuperscript{58} The CV scans for Li\textsubscript{4.4}Si and Li\textsubscript{4.4}Si@Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}\textsuperscript{-1} start from the anodic process (delithiation) and show several similar profiles for the entire processes: i) The first half-cycle shows one anodic peak at 0.66 V for Li\textsubscript{4.4}Si and 0.63 V for Li\textsubscript{4.4}Si@Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}\textsuperscript{-1}; ii) The subsequent cathodic peaks for Li\textsubscript{4.4}Si and Li\textsubscript{4.4}Si@Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}\textsuperscript{-1} are not obvious, indicating that the initial delithiation products are amorphous Si;\textsuperscript{58} iii) The subsequent anodic peaks at 0.58 V, which are less pronounced than that for Si, indicate that the previous lithiation products are amorphous Li\textsubscript{x}Si;\textsuperscript{27} and iv) The nearly identical CV profiles with cycling corroborate the superior performance of Li\textsubscript{4.4}Si and Li\textsubscript{4.4}Si@Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}\textsuperscript{-1} with respect to Si, consistent with Figure 6.5 (page 91). Note that the feature difference between the CVs and the dQ/dV plots in (Figure 6.21) can be explained by different reaction kinetics and polarization effects in the CV measurement and the galvanostatic cycling.

![Figure 6.6 Voltage profiles (A – C) and CV plots (D – F) at the scan rate of 0.1 mV/s for electrodes of Si (A and D), Li\textsubscript{4.4}Si (B and E), and Li\textsubscript{4.4}Si@Li\textsubscript{x}N\textsubscript{y}Si\textsubscript{z}\textsuperscript{-1} (C and F).](image)

To understand the charge transfer characteristics of these three materials, we employed electrochemical impedance spectroscopy (EIS). The corresponding Nyquist plots measured at the open
circuit potential (OCP) are illustrated in Figure 6.7, where the equivalent circuits fitting results are also included. The x-axis intercept represents the resistance arising from the electrode and the electrolyte solution ($R_S$). The similar $R_S$ values indicate that the electrolyte solutions in these three cases have comparable properties. In the cases of Si (Figure 6.7A) and Li$_{4.4}$Si (Figure 6.7B), one depressed semicircle is observed. In contrast, there are two depressed semicircles for Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (Figure 6.7C). These depressed semicircles can be fitted with the impedance resulting from SEI layers and electrode/electrolyte interfaces, where the former consist of $R_{SEI}$ and $CPE_{SEI}$ (CPE: constant phase element) and the latter consist of $R_{ct}$ (ct: charge transfer) and $CPE_{ct}$. Two semicircles imply two charge transfer processes (Faradaic reactions) in sequence at two different interfaces, supporting our previous conclusion that Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 is produced. The qualitatively-comparable values of $R_{SEI}$ and $R_{ct}$ for these three materials indicate that the electrochemical characteristics of Si and Li$_{4.4}$Si electrodes are essentially the same, as expected. The small value of $R_{ct}$ can be explained by small thickness and high conductivity of the Li$_x$N$_y$Si$_z$ layer. The linear portion at low frequency is attributed to the Warburg impedance (W), the lithium diffusion resistance in the electrode.

Figure 6.7 The experimental EIS spectra (blue) and the fitting lines (red) for three materials: Si (A), Li$_{4.4}$Si (B), and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (C) at open circuit potential; the equivalent circuit models are listed above each specific figure.

6.5.5 The Effect of Lithium Amount in Li$_x$Si ($x = 3.75$ and 2.33)

To investigate if the cycling performance depends on the initial Li amount in Li$_x$Si as indicated in the Introduction, we further prepared two Li$_x$Si materials with lower lithium content ($x = 3.75$ and 2.33). The XRD results and SEM images in Figure 6.22 (page 107) illustrate that the synthesized materials are phase pure and have comparable morphologies as Li$_{4.4}$Si.

As Li$_{3.75}$Si and Li$_{2.33}$Si are not fully lithiated, the initial electrochemical process could be either delithiation (charging) or lithiation (discharging), which would result in volume contraction and volume expansion, respectively. Thus, one fundamentally interesting question arises: Does the cycling performance depend on the initial treatment? The results in Figure 6.8, with Li$_{4.4}$Si as
comparison, show that the capacity and cyclability are not affected by how the initial treatment starts. This result implies that the delithiation (volume contraction) and lithiation (volume expansion) processes probably cause comparable damage to the electrode materials, as supported by the SEM images (Figure 6.23 on page 108) taken after the first half cycle of lithiation or delithiation, which show similar morphologies. For Li$_{4.4}$Si, the initial non-zero capacity when lithiation first (B) can be assigned to two reasons: i) prior self-delithiation due to different chemical potentials between Li$_{4.4}$Si and the environment; ii) in-situ SEI formation. Comparing these three materials shows that their electrode performance follows the order of Li$_{4.4}$Si > Li$_{3.75}$Si > Li$_{2.33}$Si. This trend supports the principle stated in the Introduction about the capability of Li$_x$Si to create void space after delithiation processes for accommodating lithiation processes. It is also well consistent with the experimental confirmation by Nishihara et al.$^{62}$ that the void-space engineering factor ($\epsilon$, $\epsilon$ = ($V_{Si}$ + $V_{void}$)/$V_{Si}$) for the best electrode performance is 4.1, which perfectly matches with the volume ratio of Li$_{4.4}$Si vs. Si.

![Figure 6.8](image_url) Figure 6.8 Plots of the specific capacity against the cycle number to compare the performance of Li$_{4.4}$Si, Li$_{3.75}$Si and Li$_{2.33}$Si with delithiation first (A) and lithiation first (B).

The CV results in Figure 6.9 (page 95) show that, regardless of delithiation first or lithiation first, Li$_{3.75}$Si (A and B) and Li$_{2.33}$Si (C and D) behave similarly with comparable profiles. However, the anodic peak during the first delithiation process in the case of Li$_{2.33}$Si occurs at a higher potential than for Li$_{3.75}$Si and Li$_{4.4}$Si, that is, ~0.72 V vs. ~0.65 V. This implies that Li$_{2.33}$Si needs to overcome a higher over-potential to realize the formation of amorphous Si, and that the delithiation processes of Li$_{3.75}$Si and Li$_{4.4}$Si do not involve Li$_{2.33}$Si as an intermediate.
Figure 6.9 CV plots for Li$_{3.75}$Si (A and B) and Li$_{2.33}$Si (C and D) with delithiation first (A and C) and lithiation first (B and D).

6.6 Conclusions

We have studied the potential of using lithium silicide nanoparticles (Li$_x$Si NPs, x = 4.4, 3.75, and 2.33) as anode materials for advanced batteries. All materials exhibit superior performance to Si. Because they are pre-lithiated and can naturally create void space around each NP after the initial delithiation, in principle these materials hold the promise for preventing the volume fluctuation-induced electrode damage, with Li$_{4.4}$Si as the ideal candidate. Our study confirms the superiority of Li$_{4.4}$Si to Li$_{3.75}$Si and Li$_{2.33}$Si in terms of both capacity and cyclability. In the latter two systems, we observe that the cycling performance is not affected by whether the initial treatment starts with delithiation (charging first) or lithiation (discharging first). The biggest challenge confronting the development of high-performance anodes using Li$_x$Si NPs is their high reactivity, making it difficult to directly protect them with robust and conductive shells. Nevertheless, we have demonstrated the concept by protecting the surface of Li$_{4.4}$Si with a nitride layer that is created via ball-milling assisted surface nitridation. The obtained Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$ materials show improved cyclability, which enhances with the increase of nitridation extent despite the tradeoff of decreased capacity. We think the surface nitridation can serve as a base for the subsequent construction of more effective shells. Overall, this study demonstrates the promises and challenges of developing lithium silicide anodes of high performance for advanced batteries.
6.7 References


(20) Lv, Q., Liu, Y., Ma, T., Zhu, W., and Qiu, X., "Hollow Structured Silicon Anodes with Stabilized Solid Electrolyte Interphase Film for Lithium-Ion Batteries". *ACS Applied Materials & Interfaces* 2015, 7(42), 23501-23506.


### 6.8 Supporting Information

![Figure 6.10 Characterizations of commercial Si micropowder by XRD (A), EDS (B), and SEM (the inset in B).](image)

Figure 6.10 Characterizations of commercial Si micropowder by XRD (A), EDS (B), and SEM (the inset in B).
Figure 6.11 Representative STEM images of Li$_{4.4}$Si and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 with numbered boxes indicating areas where EDS measurements shown in Table 6.1 were quantified.

Table 6.1 Normalized quantification, averages, and standard deviations of silicon and nitrogen content from EDS measurements, as indicated in Figure 6.11. Oxygen (from air exposure of sample), carbon (from support film), and iron (from ball milling) are omitted.

<table>
<thead>
<tr>
<th>Area</th>
<th>Li$_{4.4}$Si</th>
<th>Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At. %</td>
<td>Wt. %</td>
</tr>
<tr>
<td>Si</td>
<td>88.9</td>
<td>94.2</td>
</tr>
<tr>
<td>N</td>
<td>11.1</td>
<td>5.8</td>
</tr>
<tr>
<td>Si</td>
<td>85.7</td>
<td>92.3</td>
</tr>
<tr>
<td>N</td>
<td>14.3</td>
<td>7.7</td>
</tr>
<tr>
<td>Si</td>
<td>82.6</td>
<td>90.5</td>
</tr>
<tr>
<td>N</td>
<td>17.4</td>
<td>9.5</td>
</tr>
<tr>
<td>Si</td>
<td>88.5</td>
<td>93.9</td>
</tr>
<tr>
<td>N</td>
<td>11.5</td>
<td>6.1</td>
</tr>
<tr>
<td>Si</td>
<td>91.2</td>
<td>95.4</td>
</tr>
<tr>
<td>N</td>
<td>8.8</td>
<td>4.6</td>
</tr>
<tr>
<td>Si</td>
<td>94.4</td>
<td>97.1</td>
</tr>
</tbody>
</table>
Table 6.1 Continued

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>5.6</td>
<td>2.9</td>
<td>15.4</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>7</td>
<td>94.4</td>
<td>97.1</td>
<td>7</td>
<td>80.8</td>
</tr>
<tr>
<td>N</td>
<td>5.6</td>
<td>2.9</td>
<td>19.2</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>8</td>
<td>94.7</td>
<td>97.3</td>
<td>8</td>
<td>74.6</td>
</tr>
<tr>
<td>N</td>
<td>5.3</td>
<td>2.7</td>
<td>25.4</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>9</td>
<td>92.1</td>
<td>95.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>7.9</td>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>avg</td>
<td>90.3</td>
<td>94.9</td>
<td>avg</td>
<td>79.2</td>
</tr>
<tr>
<td>N</td>
<td>9.7</td>
<td>5.1</td>
<td>20.8</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>stdev</td>
<td>3.98</td>
<td>stdev</td>
<td>4.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar ratio of N/Si</td>
<td>avg</td>
<td>0.11</td>
<td>avg</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>stdev</td>
<td>0.04</td>
<td>stdev</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.12 EDS elemental mapping of Li₄Si. (A) HAADF image showing the area measured; (B) Si mapping; (C) N mapping; (D) O mapping; (E) Overlay of Si and N; (F) Overlay of HAADF image and Si signal; (G) Overlay of HAADF image and N signal; and (H) Overlay of HAADF image and O signal.
Figure 6.13 EDS elemental mapping of Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1. (A) HAADF image showing the area measured; (B) Si mapping; (C) N mapping; (D) O mapping; (E) Overlay of Si and N; (F) Overlay of HAADF image and Si signal; (G) Overlay of HAADF image and N signal; and (H) Overlay of HAADF image and O signal.

Figure 6.14 FFT analysis from HRTEM of the amorphous edge layer (blue solid lines) and inner crystalline material (red dashed lines) of Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1.

Figure 6.15 EDS spectra of Si (A), Li$_{4.4}$Si (B), and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (C) with the wt% and at% of the respective elements and the molar ratio of N/Si. These data were obtained when taking the SEM images in Figure 6.1.
Figure 6.16 Cycle performance (A) and Coulombic efficiency (B) of electrodes using commercial Si materials. In each figure, the conditions used to prepare the electrode mixture are compared, non-ball milled 80 wt% active materials with 12 wt% AB, and 8 wt% PVDF (black) and ball milled 64 wt% active materials with 28 wt% AB and 8 wt% PVDF (red).

Table 6.2 Comparison of various studies of Li$_x$Si for battery applications.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weydanz$^{35}$</th>
<th>Shigematsu$^{38}$</th>
<th>Tang$^{39}$</th>
<th>Nishihara$^{37}$</th>
<th>Pan$^{36}$</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Li$_4$Si</td>
<td>Li$_4$Si</td>
<td>LiSi</td>
<td>Li$_4$Si</td>
<td>Li$_{1.7}$Si</td>
<td>Li$_4$Si</td>
</tr>
<tr>
<td></td>
<td>1 MLiPF$_6$/PC-EC-DMC (1:1:3)</td>
<td>1 MLiPF$_6$/EC-DMC (1:1:3)</td>
<td>1 MLiPF$_6$/EC-DMC (1:1)</td>
<td>1 MLiPF$_6$/EC-DMC (1:1)</td>
<td>1 MLiPF$_6$/EC-DEC (1:1)</td>
<td>1 MLiPF$_6$/EC-DEC (1:1)</td>
</tr>
<tr>
<td>Wt% of Active Material</td>
<td>NA</td>
<td>80</td>
<td>70</td>
<td>100</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Cycling Rate</td>
<td>0.016 C</td>
<td>NA</td>
<td>0.03 C</td>
<td>0.03 C</td>
<td>0.03 C</td>
<td>0.10 C</td>
</tr>
<tr>
<td>Potential Window</td>
<td>0.02 – 0.7 V vs. E$_{Li/Li^+}$</td>
<td>0.01 – 0.8 V vs. E$_{Li/Li^+}$</td>
<td>0.01 – 2.5 V vs. E$_{Li/Li^+}$</td>
<td>0.01 – 1.5 V vs. E$_{Li/Li^+}$</td>
<td>0.02 – 2.0 V vs. E$_{Li/Li^+}$</td>
<td>0.05 – 1.0 V vs. E$_{Li/Li^+}$</td>
</tr>
<tr>
<td>Initial Capacity</td>
<td>981 mAh/g-Si</td>
<td>1357 mAh/g-Si</td>
<td>870 mAh/g-Si</td>
<td>3125 mAh/g-Si</td>
<td>2900 mAh/g-Si</td>
<td>2384 mAh/g-Si</td>
</tr>
<tr>
<td>Capacity at #th Cycle</td>
<td>626 mAh/g-Si at 10th cycle</td>
<td>77 mAh/g-Si at 4th cycle</td>
<td>805 mAh/g-Si at 10th cycle</td>
<td>2083 mAh/g-Si at 10th cycle</td>
<td>2450 mAh/g-Si at 10th cycle</td>
<td>1132 mAh/g-Si at 10th cycle</td>
</tr>
</tbody>
</table>

*PC: propylene carbonate; EC: ethylene carbonate; DEC: diethyl carbonate; DMC: dimethyl carbonate, NA: not available;
Figure 6.17 Plots of specific charging capacity (solid symbols) and discharging capacity (open symbols) against the cycle number for Li_{4.4}Si@Li_{x}N_{y}Si_{z-3}.

Figure 6.18 SEM (C and D) and EDS (A and B) characterizations of Li_{4.4}Si@Li_{x}N_{y}Si_{z-2} (A and C) and Li_{4.4}Si@Li_{x}N_{y}Si_{z-3} (B and D).
Figure 6.19 Comparison of the cycling performance of Li$_{4.4}$Si (A) and Li$_{4.4}$Si@Li$_{3}$N$_{x}$Si$_{y}$ (B) electrodes made by three different processes: (black) no ball milling, 80 wt% active materials with 12 wt% AB, and 8 wt% PVDF; (blue) ball milled, 80 wt% active materials with 12 wt% AB, and 8 wt% PVDF; (red) ball milled, 64 wt% active materials with 28 wt% AB and 8 wt% PVDF.

Figure 6.20 The electrochemical analysis of electrode prepared from untreated commercial Si micropowder (ball milled 64 wt% active material with 28 wt% AB and 8 wt% PVDF). (A) voltage profiles; (B) dQ/dV plots; (C) CV results; and (D) EIS spectrum.
Figure 6.21 The dQ/dV plots for electrodes of Si (A), Li$_{4.4}$Si (B) and Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$-1 (C).

Figure 6.22 XRD results (A and B) and SEM images (C and D) of Li$_{3.75}$Si (A and C) and Li$_{2.33}$Si (B and D).
Figure 6.23 SEM images to study the possible morphological changes of Li$_{3.75}$Si and Li$_{2.33}$Si after the initial lithiation or delithiation. Pristine synthesized Li$_{3.75}$Si (A); DEC cleaned anode of Li$_{3.75}$Si after the first half cycle of delithiation (B), and that after the first half cycle of lithiation (C); pristine synthesized Li$_{2.33}$Si (D); DEC cleaned anode of Li$_{2.33}$Si after the first half cycle of delithiation (E), and that after the first half cycle of lithiation (F).
CHAPTER 7
CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

In conclusion, this thesis has systematically studied two systems of lithiated or sodiated electrode materials for the development of next generation of rechargeable batteries, that is, metal sulphides (M_2S, M=Na or Li) as alternatives for sulfur cathodes and lithium silicides (Li_xSi) as alternatives for silicon anodes.

Phase-pure, anhydrous M_2S nanocrystals are synthesized via a novel method, that is, reacting hydrogen sulfide (H_2S) gas with alkali metals (M) that are introduced in the form of metalorganic complexes in organic solutions. The synthetic process is thermodynamically favorable, spontaneous, and irreversible at ambient temperature and pressure, proceeding to completion rapidly. Specifically, two sets of metalorganic complexes are used: alkali metal naphthalenides (M-NAP) and alkali metal alkoxides (ROM). M_2S nanocrystals with tunable morphologies can be obtained by changing the metalorganic agent and/or the solvent. The synthesized lithium sulfide (Li_2S) nanocrystals show superior electrode performance than the commercial Li_2S in terms of specific capacity, cycling stability, output voltage and voltage efficiency. When using ROM for the M_2S synthesis, all auxiliary reagents can be directly recycled for the subsequent rounds of synthesis, by adding new M to react with the regenerated alcohol to replenish ROM and cogenerate hydrogen gas (H_2). As a result, the realized net reaction is H_2S + 2M \rightarrow M_2S + H_2, which abates a chemical waste (H_2S), produces the wanted battery materials (M_2S), and recovers the hydrogen atoms in H_2S in the form of H_2 gas.

Li_xSi nanocrystals (x = 4.4, 3.75, and 2.33), three thermodynamically stable phases, are synthesized via high-energy ball milling. All three materials exhibit superior performance to Si, with Li_4.4Si as the optimum candidate. The enhancement is due to their pre-lithiation state, which enables generating void space around Li_xSi particles after the initial electrochemical delithiation to accommodate the subsequent, inevitable volume fluctuation. Ultimately, the development of high-performance Li_xSi-based anodes requires encapsulating them inside robust and conductive shells. However, the high reactivity of Li_xSi makes it very challenging to directly create such protective shells. Alternatively, we have demonstrated the concept qualitatively by stabilizing the surface of Li_4.4Si with a nitride layer, which is created via ball-milling assisted surface nitridation. The produced Li_4.4Si@Li_N_ySi_z materials show improved cyclability which further enhances with the increase of nitridation extent in spite of decreased capacity. Our study demonstrates the promises and challenges of developing high-performance lithium silicide anodes for advanced batteries.
7.2 **Future Work**

Future studies for the M$_2$S project are suggested as follows:

1) It is fundamentally interesting and important to understand the nucleation/growth kinetics and the morphology tuning mechanisms. It can be pursued by ex-situ monitoring (X-ray powder diffraction, scanning electron microscope/transmission electron microscopy, and X-ray photoelectron spectroscopy) the size- and morphology-evolution of M$_2$S products by changing a series of experimental conditions, such as the ROM concentration, reaction temperature, H$_2$S gas flow rate, choice of alcohols, choice of solvents, ratio of ROM/H$_2$S, etc.

2) To achieve high-performance M$_2$S cathodes, we can explore a novel method to produce M$_2$S-core@shell structures such as M$_2$S@C and M$_2$S@conductive-polymer composites, by utilizing the wet-chemistry nature of our synthesis. The synthesis of M$_2$S@conductive-polymer composites can be implemented by adding the conductive polymer such as polypyrrole and polythiophene in the ROM solution before introducing H$_2$S. The synthesis of M$_2$S@C composites can be executed by adding a carbonizable polymer such as polyacrylonitrile (PAN) and polyvinylpyrrolidone (PVP) in the ROM solution, followed by the pyrolysis of the polymer at elevated temperatures. In both cases, M$_2$S nanocrystals are expected to be conformally encapsulated in the shell matrices, which can increase the electrode conductivity, improve the mechanical robustness, and prevent the polysulfides shuttle effect during charging and discharging processes in batteries. The composites may be prepared in the powder form by fully drying the solvent or the non-woven fiber form by partially evaporating off the solvent first and then electrospinning the concentrated solutions.

Future studies for the Li$_x$Si project are suggested as follows:

1) Comprehensive studies of the surface nitridation and the electrochemical performance of Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$ are fundamentally interesting. For instance, what is the exact composition of the nitride layer in Li$_{4.4}$Si@Li$_x$N$_y$Si$_z$? Is it a ternary composite or a mixture of Li$_3$N and Si or Si$_3$N$_4$? X-ray photoelectron spectroscopy surface analysis will be helpful for the shell composition study. Can annealing increase the crystallinity of the nitride layer and then enhance the electrode performance?

2) We think the demonstrated surface nitridation can serve as a basis for the subsequent construction of more effective shells to further improve the electrode performance. For example, the creation of resilient carbon outer shells can be attempted by dispersing Li$_x$Si@Li$_x$N$_y$Si$_z$ particles in a dimethylformamide (DMF) solution of PAN or PVP and then carbonizing the polymer after drying off DMF. The construction of Al$_2$O$_3$ or TiO$_2$ shells can be realized by atomic layer deposition (ALD). It has been demonstrated in the literature that silicon anodes coated with any of these three
materials present much enhanced electrode performance compared with the uncoated counterparts.1-3

7.3 References


APPENDIX A
PERMISSIONS FOR USE OF CHAPTERS 3 AND 4

A.1 Background

This appendix includes the permissions obtained from ChemPlusChem and ACS Applied Materials and Interfaces. In addition, the email permissions from coauthors to use the publications as Chapter 3 and Chapter 4 in the thesis are included.

A.2 Permissions

A.2.1 Chapter 3 – ChemPlusChem, Wiley

This Agreement between Xuemin Li ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

<table>
<thead>
<tr>
<th>License number</th>
<th>4083260525558</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>April 6, 2017</td>
</tr>
<tr>
<td>Licensed content publisher</td>
<td>John Wiley and Sons</td>
</tr>
<tr>
<td>Licensed content publication</td>
<td>CHEMPLUSCHEM</td>
</tr>
<tr>
<td>Licensed content title</td>
<td>Thermodynamically Favorable Conversion of Hydrogen Sulfide into Valuable Products through Reaction with Sodium Naphthalenide</td>
</tr>
<tr>
<td>Licensed content author</td>
<td>Xuemin Li, Rachel M. Morrish, Yuan Yang, Colin A. Wolden, Yongan Yang</td>
</tr>
<tr>
<td>Licensed content date</td>
<td>Jul 23, 2015</td>
</tr>
<tr>
<td>Licensed content pages</td>
<td>5</td>
</tr>
<tr>
<td>Type of use</td>
<td>Dissertation/Thesis</td>
</tr>
<tr>
<td>Requestor type</td>
<td>Author of this Wiley article</td>
</tr>
<tr>
<td>Format</td>
<td>Electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>Full article</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----</td>
</tr>
<tr>
<td>Title of your thesis / dissertation</td>
<td>Development of Advanced Electrode Materials for Next Generation of Rechargeable Batteries</td>
</tr>
<tr>
<td>Expected completion date</td>
<td>May 2017</td>
</tr>
<tr>
<td>Expected size (number of pages)</td>
<td>140</td>
</tr>
</tbody>
</table>
| Requestor location | Xuemin Li  
1012 14th Street  
GOLDEN, CO 80401  
United States  
Attn: Xuemin Li |
| Publisher tax ID | EU826007151 |
| Billing type | Invoice |
| Billing address | Xuemin Li  
1012 14th Street  
GOLDEN, CO 80401  
United States  
Attn: Xuemin Li |
| Total | 0.00 USD |

**TERMS AND CONDITIONS**

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., "CCC's Billing and Payment terms and conditions"),
Terms and Conditions

• The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

• You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, and any CONTENT (PDF or image file) purchased as part of your order, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

• With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

• The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that
you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto.

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
• The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

• This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

• Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

• These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

• In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

• WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

• This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

• This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under
the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License: The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License: The Creative Commons Attribution Non-Commercial (CC-BY-NC) License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. (see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License: The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations: Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee. Further details can be found on Wiley Online Library: http://olabout.wiley.com/WileyCDA/Section/id-410895.html.

A.2.2 Chapter 4 – ACS Applied Materials & Interfaces, American Chemical Society

Title: Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries

Author: Xuemin Li, Colin A. Wolden, Chunmei Ban, and Yongan Yang

Publication: ACS Applied Materials & Interfaces

Publisher: American Chemical Society

American Chemical Society’s Policy on Theses and Dissertations

If your university requires you to obtain permission, you must use the RightsLink permission system. See RightsLink instructions at http://pubs.acs.org/page/copyright/permissions.html.

This is regarding request for permission to include your paper(s) or portions of text from your paper(s) in your thesis. Permission is now automatically granted; please pay special attention to the implications paragraph below. The Copyright Subcommittee of the Joint Board/Council Committees on Publications approved the following:

Copyright permission for published and submitted material from theses and dissertations: ACS extends blanket permission to students to include in their theses and dissertations their own articles, or portions thereof, that have been published in ACS journals or submitted to ACS journals for publication, provided that the ACS copyright credit line is noted on the appropriate page(s).
Publishing implications of electronic publication of theses and dissertation material: Students and their mentors should be aware that posting of theses and dissertation material on the Web prior to submission of material from that thesis or dissertation to an ACS journal may affect publication in that journal. Whether Web posting is considered prior publication may be evaluated on a case-by-case basis by the journal’s editor. If an ACS journal editor considers Web posting to be “prior publication”, the paper will not be accepted for publication in that journal. If you intend to submit your unpublished paper to ACS for publication, check with the appropriate editor prior to posting your manuscript electronically.

Reuse/Republication of the Entire Work in Theses or Collections: Authors may reuse all or part of the Submitted, Accepted or Published Work in a thesis or dissertation that the author writes and is required to submit to satisfy the criteria of degree-granting institutions. Such reuse is permitted subject to the ACS’ “Ethical Guidelines to Publication of Chemical Research” (http://pubs.acs.org/page/policy/ethics/index.html); the author should secure written confirmation (via letter or email) from the respective ACS journal editor(s) to avoid potential conflicts with journal prior publication*/embargo policies. Appropriate citation of the Published Work must be made. If the thesis or dissertation to be published is in electronic format, a direct link to the Published Work must also be included using the ACS Articles on Request author-directed link – see http://pubs.acs.org/page/policy/articlesonrequest/index.html

* Prior publication policies of ACS journals are posted on the ACS website at http://pubs.acs.org/page/policy/prior/index.html

If your paper has not yet been published by ACS, please print the following credit line on the first page of your article: "Reproduced (or 'Reproduced in part') with permission from [JOURNAL NAME], in press (or 'submitted for publication'). Unpublished work copyright [CURRENT YEAR] American Chemical Society." Include appropriate information.

If your paper has already been published by ACS and you want to include the text or portions of the text in your thesis/dissertation, please print the ACS copyright credit line on the first page of your article: “Reproduced (or 'Reproduced in part') with permission from [FULL REFERENCE CITATION.] Copyright [YEAR] American Chemical Society." Include appropriate information.

Submission to a Dissertation Distributor: If you plan to submit your thesis to UMI or to another dissertation distributor, you should not include the unpublished ACS paper in your thesis if the thesis will be disseminated electronically, until ACS has published your paper. After publication of the paper by ACS, you may release the entire thesis (not the individual ACS article by itself) for electronic dissemination through the distributor; ACS’s copyright credit line should be printed on the first page of the ACS paper.

You have been directed to this webpage as a result of the type of license signed between the author and the American Chemical Society that provides users with some different terms of use.
Open Access Articles:
For articles marked “Terms of Use CC-BY”, please see Terms of Use CC-BY
For articles marked “Terms of Use CC-BY-NC-ND”, please see Terms of Use CC-BY-NC-ND
For articles marked only with an ACS AuthorChoice logo, please see Terms of Use

Inquiries about open access articles only should be addressed to Darla Henderson, Ph.D., Asst. Director, Open Access Programs.

Public Domain and Crown Copyright, and Other Articles: For articles in the public domain: Check the copyright notice that appears with the abstract or on the first page of the article/chapter. An article is in the public domain if all of the authors of the article worked for the U.S. Government when the article was written. Requesters who want to use material that appeared in articles that are in the public domain do not need permission if the notice on the article/chapter states, “Not subject to U.S. Copyright,” and credit to another source does not appear in the figure/table caption, if you are using figures/tables from the article.

For articles subject to “Crown” copyright: Check the notice that appears with the abstract or on the first page of the article/chapter. If all of the authors of a requested article worked for the governments of Australia, Canada, or the United Kingdom when the article was written, a “Crown” copyright notice appears. Write directly to the authors of the article for permission because the authors’ countries own copyright to the article.

For other articles not recognized by RightsLink or the ACS article delivery system: If the solutions above do not apply, it’s possible the error is with the article delivery system. Send your request directly to the ACS Copyright Office at copyright@acs.org. Send a permission request that includes a complete reference citation, the amount of material you want to use from the article/chapter (such as the specific ACS figure numbers), and where you plan to reuse the ACS material. Include your complete mailing address, your 24-hour fax number, and the specific deadline by which you need to receive our response.
A.3 Email correspondence from coauthors

A.3.1 Email for Chapter 3

Emails from coauthors were received in response to the following email sent at 9:53 am on April 3, 2017:

Dear all,

As a coauthor [Li, X.; Morriseh, R. M.; Yang, Y.; Wolden, C. A.; Yang, Y.; Thermodynamically Favorable Conversion of Hydrogen Sulfide into Valuable Products through Reaction with Sodium Naphthalenide. ChemPlusChem 2015, DOI: 10.1002/cplu.201500299] you are receiving this email because I require a response from each of you regarding the written consent for the use of the paper in my Ph. D. thesis. If you receive another email similar to this one, please respond to each individually.

In accordance with the protocols for including published and accepted papers in a thesis, I am required to obtain written consent from all coauthors. Could you please reply to me with your consent regarding "Thermodynamically Favorable Conversion of Hydrogen Sulfide into Valuable Products through Reaction with Sodium Naphthalenide".

Here is an example response:

"I, [your name here] hereby authorize Xuejin Li to use any or all of "Thermodynamically Favorable Conversion of Hydrogen Sulfide into Valuable Products through Reaction with Sodium Naphthalenide" in her published thesis."

Thank you very much for your cooperation!

Regards,

Xuejin Li
Department of Chemistry
Colorado School of Mines

The following responses were received regarding this email:
A.3.2 Email for Chapter 4

Emails from coauthors were received in response to the following email sent at 9:57 am on April 3, 2017:

---

**Yuan Yang**

to me  

I, (Yuan Yang) hereby authorize Xuemin Li to use any or all of “Thermodynamically Favorable Conversion of Hydrogen Sulfide into Valuable Products through Reaction with Sodium Naphthalenedi” in her published thesis.

Best,
Yuan Yang

---

**Yongan Yang**

to me  

Xuemin,

“I, Yongan Yang, hereby authorize Xuemin Li to use any or all of “Thermodynamically Favorable Conversion of Hydrogen Sulfide into Valuable Products through Reaction with Sodium Naphthalenedi” in her published thesis.”

---

**Xuemin Li**

to Chunnai, Colin, Yongan

Dear all,

As a coauthor (Li, X.; Wolden, C. A.; Ban, C.; Yang, Y. Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries. ACS Applied Materials & Interfaces 2015, DOI: 10.1021/acsami.5b09357) you are receiving this email because I require a response from each of you regarding the written consent for the use of the paper in my Ph. D. thesis. If you receive another email similar to this one, please respond to each individually.

In accordance with the protocols for including published and accepted papers in a thesis, I am required to obtain written consent from all coauthors. Could you please reply to me with your consent regarding “Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries”

Here is an example response:

“I, (your name here) hereby authorize Xuemin Li to use any or all of “Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries” in her published thesis.”

The following responses were received regarding this email:

---

**Colin Wolden**

to me  

I, Colin Wolden hereby authorize Xuemin Li to use any or all of “Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries” in her published thesis.

From: Xuemin Li [xuli@umn.edu]
Sent: Monday, April 03, 2017 9:57 AM
To: Sun, Chunnai; Colin Wolden; Yongan Yang
Subject: Request for publication permissions-Xuemin’s thesis

---

**Yongan Yang**

to me  

Xuemin,

“I, Yongan Yang, hereby authorize Xuemin Li to use any or all of “Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries” in her published thesis.”

Yongan
Hi Xuemin,

I, Chunmei Ban, hereby authorize Xuemin Li to use any or all of “Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries” in her published thesis.

Chunmei

122