IRON PYRITE NANOCRYSTALS: SYNTHESIS AND APPLICATIONS IN LITHIUM ION BATTERIES

by
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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).

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Iron pyrite (FeS$_2$) has been widely utilized as a commercial cathode material for lithium ion batteries (LIBs) for 30+ years, due to its high charge capacity, natural abundance, low cost, and non-toxicity. Industrialized versions include both non-rechargeable Li/FeS$_2$ batteries at ambient temperatures of -40 – 60 °C and the rechargeable Li/FeS$_2$ batteries at high-temperatures of 400 – 450 °C. However, FeS$_2$ cathodes suffer from poor cyclability at room temperature due to multiple issues, including volume-fluctuation induced electrode pulverization, detrimental reactions between the electrolyte solution and the active materials, and the formation of soluble lithium polysulfides. One promising strategy to overcome these challenges is the encapsulation of synthetic FeS$_2$ nanocrystals in a conductive, resilient carbon (RC) matrix.

We have studied two approaches for producing the RC matrix, using glucose or polyacrylonitrile as the carbon source. The glucose-based FeS$_2$@RC composite is fabricated through a hydrothermal treatment followed by a pyrolysis treatment. The polyacrylonitrile-based FeS$_2$@RC composite is produced by directly pyrolyzing the FeS$_2$/polyacrylonitrile slurry. The FeS$_2$@RC electrodes showed superior cyclability compared with the FeS$_2$ electrodes, due to the enhanced capability to accommodate the volume fluctuation.

Moreover, to achieve conformal encapsulation and prevent particle aggregation, monodisperse, colloidal iron pyrite nanocrystals (or FeS$_2$ NC inks, 5.5 ± 0.3 nm) have been synthesized via a facile, air-compatible method. Inks are desirable for large scale manufacturing processes such as roll-to-roll deposition or ink-jet printing. The synthesis combines a solvothermal pre-synthesis and a digestive ripening post-process. Density Functional Theory computations on the precursor suggest an acid mediated degradation mechanism for the formation of FeS$_2$ nanocrystals.
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<td>CV</td>
<td>cyclic voltammetry</td>
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<tr>
<td>DDA</td>
<td>dodecylamine</td>
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<td>DMF</td>
<td>dimethylformamide</td>
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<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<td>EDX</td>
<td>energy-dispersive x-ray spectroscopy</td>
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<td>FeE₃</td>
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CHAPTER 1
GENERAL INTRODUCTION

Given the increasing global demand and rising costs of energy, as well as the US over-reliance on foreign sources of fossil fuels and their inherent environmental issues, it is widely accepted that renewable energy technologies are paramount. Photovoltaics, biofuels, fuel cells, hydroelectric, and wind energy have been increasingly explored in the past decades. Alongside energy generation technologies, energy storage is additionally important. With the rise in popularity of battery-powered devices, such as laptops and cell phones, there is a need to reform current battery technologies by developing more rechargeable batteries that are cost-effective, environmentally benign, and safe, in addition to the conventional requirements of high charge capacity, energy density, power density, and cyclability.¹

1.1 Batteries

The battery is unrivaled as an electrochemical energy storage device. They are grouped as either “primary,” or non-rechargeable, and “secondary,” or rechargeable devices. The general design of a battery consists of a negative (anode) and positive (cathode) electrode pair, with a negative ΔG between them resulting in a spontaneous, energy producing reaction. While fuel cells directly produce electrical energy by oxidizing a fuel, such as hydrogen, batteries store energy produced from another method. Rechargeable batteries operate by utilizing external energy to drive a reaction on each electrode against its free energy gradient, or charging the battery, and storing the energy until needed.² When a circuit is completed, the battery is discharged, that is, the anode material is oxidized and the cathode material is simultaneously reduced. Electrons flow through an external wire, powering a device, while ions travel internally through an electrolyte solution to balance the charge. For instance, commercial Ni-Cd rechargeable batteries utilize cadmium anodes and nickel oxyhydroxide cathodes:

\[ Cd + 2HO^- \rightarrow Cd(OH)_2 + 2e^- \]  

Equation 1.1 shows the oxidation of cadmium to cadmium hydroxide on the anode, and Equation 1.2 shows the reduction of nickel oxyhydroxide to nickel hydroxide on the cathode, during discharge. The hydroxide ions flow the reverse direction as the electrons, thus preventing a build up of negative charge. The overall reaction can be summarized in Equation 1.3 as

\[ 2NiO(OH) + Cd + 2H_2O \rightleftharpoons 2Ni(OH)_2 + Cd(OH)_2 \]  

with the forward reaction representing discharging, and the reverse reaction representing charging.
The Ni-Cd battery is only one example of a commercial battery. Many commercial batteries are available, with each having certain advantages. Typically, cells are commercially available in either ~1.5V or ~3.5V varieties. Existing batteries (Pb/H₂SO₄, Ni/MH, and Ni/Cd) in cars are all based on 1.5-V unit cells. Some have exceptional energy- and power-densities, such as Si/Li₂S, Li/O₂, Na-ion, and Mg-ion batteries. No one battery is suitable for all situations. For example, thermal batteries are high temperature (>400 °C) cells that use molten salts as an electrolyte in contrast to a solution. Primary versions are stored at room temperature, thus providing an indefinite shelf life, as the salts are solid and inactive until heated. Once heated by an internal pyrotechnic heat source, the salt melts. As an electrolyte, molten salts have very high ionic conductivities and therefore are able to release their charge quickly, resulting in high power. These cells are useful for military purposes, usually in guided weapons systems. Other practical applications include pacemakers, which need long lifetimes and small size, and submarines or wind farms, which must be large and rechargeable.

The most successful secondary battery system is the lithium ion battery (or LIB), which was commercialized in the 1990s. Lithium is the lightest metal, enabling an exceptionally high energy density. LIBs based on Li/CoO₂ are widely utilized in portable electronics due to their good cycling life and low weight. However, despite the variety of available batteries, and the improvements made in the last 30 years, many issues still arise. One promising technique being studied is the possibility of converting the existing non-rechargeable batteries – Li/FeS₂, for instance – to rechargeable batteries, through the use of protective coatings, alternative electrolytes, or dopants. One benefit to this strategy is that little change in the infrastructure is required due to previous industrialization.

1.2 Iron pyrite

Iron pyrite, more commonly known as “fool’s gold,” is a mineral with the formula FeS₂ that has been researched extensively for its useful properties for applications in photovoltaics and LIBs. The crystal structure is similar to the rock-salt (or NaCl) structure, with two interlaced face-centered cubic (fcc) lattices of Fe²⁺ ions and S₂²⁻ pairs. Since the 1980s FeS₂ has been utilized as a cathode material in batteries, including rechargeable (secondary) LIBs at high temperatures (400 °C) and non-rechargeable (primary) lithium batteries at ambient temperatures (-40 to 60 °C). Over the same time period FeS₂ has also been extensively studied as a semiconductor photoabsorber due to the fact that its band gap (E₅) is in the optimal range of 0.90 ~ 1.5 eV for single-junction photovoltaic devices. These properties, combined with its non-toxicity, environmental benignity, potential low cost, and the natural abundance of iron and sulfur make FeS₂ an attractive material for contributing to a clean and renewable energy-based society.
FeS$_2$ has a number of attractive properties as a semiconductor photoabsorber. Its band gap is 0.95 eV, in the optimal range for single-junction photovoltaic devices according to the Shockley-Queisser limit. Despite its indirect band gap, which typically has less efficient electron excitation than a direct band gap, FeS$_2$ has a high absorption coefficient ($\varepsilon$) of $6.5 \times 10^5$ cm$^{-1}$, reflecting its good conductivity. Furthermore, it exhibits a large electron diffusion length of 100 – 1000 nm, which is highly desirable for charge separation and transport. Together, these features enable strong absorption in the visible range.

In battery applications, FeS$_2$ has been used as an anode with LiCoO$_2$ and as a cathode with Li or Na. In LIBs, FeS$_2$ has a higher energy density (1270 mW•h/g) than the currently-prevailing C/LiCoO$_2$ LIBs (850 mW•h/g). It incorporates lithium in two steps:

$$FeS_2 + 2Li^+ + 2e^- \rightarrow Li_2FeS_2$$

(1.4)

$$Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow Fe^0 + 2Li_2S$$

(1.5)

At elevated temperatures (400-450 °C), each FeS$_2$ is able to reversibly react with four Li ions according to Equations 1.4 and 1.5, utilizing the full theoretical capacity of 890 mAh/g. Argonne and Sandia National Labs developed high temperature batteries for military purposes in the 1990s. However, at room temperature a maximum of 2.8 Li ions can be reversibly cycled, as described in Equation 1.6:

$$Li_{2-x}FeS_2 + (2 + x)Li^+ + (2 + x)e^- \rightarrow Fe^0 + 2Li_2S \quad (0 < x \leq 0.8)$$

(1.6)

The consequence is a ≥30% irreversible capacity loss after the first cycle. Even worse, fewer Li$^+$ ions are extracted in each subsequent cycle and the cell fails after a few cycles. Consequently, commercial FeS$_2$ batteries for use at ambient temperatures are non-rechargeable. In fact, FeS$_2$ has a strong history in primary lithium batteries at room temperature – 1.5 V Li/FeS$_2$ primary batteries have been sold by Energizer Inc. (previously the Eveready Battery Company) since 1989. Nonetheless, the challenge of converting it to a rechargeable material has been on-going for decades.

The charge-discharge mechanism and the underlying causes for the poor cyclability of FeS$_2$ have been investigated by several groups. Scherson et al. applied in situ fluorescence X-ray absorption near edge spectroscopy (XANES) and X-ray absorption fine structure (XAFS) to study the electronic and structural properties of FeS$_2$ electrodes when fully discharged and subsequently half-re-charged. After observing both sulfur and iron K-edge signals, they concluded that the spectral signatures were consistent with Li$_2$FeS$_2$. Peled et al. employed X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD) and electrochemical methods, concluding that the slow diffusion rate of iron cations through Li$_2$FeS$_2$ limits the reaction rate and causes an overpotential. They also observed an improved capacity from 7 nm particles compared to 40 µm particles when cycling between 1.6 – 1.85 V vs. Li$^+$/Li (the charge region of Li$_2$FeS$_2$). Fong et al. used in-situ XRD and in-situ Fe Mossbauer spectroscopy to
observe the electrochemistry and chemistry of cells cycled near room temperature. They observed a temperature and rate dependence on lithiation processes due to the slow diffusion of lithium in bulk FeS$_2$, and the formation of pyrrhotite (orthorhombic FeS$_y$, where $y = 1.064$) and sulfur at high voltages upon delithiation at room temperature. Overall, four critical challenges remain for the poor cyclability of FeS$_2$ cathode: 1) poor conductivity of Li$_2$S$^-$, 2) detrimental reactions between the electrode material and electrolyte solution; 3) volume fluctuations causing mechanical stress and a resulting loss of contact with the current collector; and 4) the formation of soluble lithium polysulfides (Li$_2$S$_n$, $n > 2$).

The degradation mechanism of FeS$_2$ electrodes is summarized in Figure 1.1. During the first discharge (step 1), FeS$_2$ is lithiated to form Fe and Li$_2$S – a process that results in a volume expansion up to 260% (or $V_{\text{Final}} = 2.6 V_{\text{Initial}}$). Simultaneously, interactions between the electrolyte solution and the electrode material result in the irreversible formation of a cathode electrolyte interphase (CEI). The CEI formation has several consequences, consuming both active material and lithium, and insulating the electrode surface. The following charge (step 2) partially delithiates the material, removing a maximum of 2.8 Li ions and resulting in Li$_{2-x}$FeS$_2$ ($x \leq 0.8$). The mechanical stress from the volume fluctuation can crack both the CEI and the crystals of active material. Moreover, polysulfides are also formed, which present a serious problem in addition to their poor electrical and ionic conductivity ($1 \times 10^{-13}$ S/cm).

Polysulfides are soluble in the electrolyte solution and thus can diffuse across the separator, be reduced to lower-order polysulfides (Li$_2$S$_{n-x}$) on the anode and then oxidized again to higher-order polysulfides (Li$_2$S$_n$) on the cathode. This repeated travel between the anode and the cathode, called the “shuttle effect”, causes a continuous loss of the electrode material in the forms of Li$_2$S$_{n-x}$ deposited on the anode and Li$_2$S$_n$ soluble in the solution. During continued cycling (step 3), electrode material is continuously lost into the electrolyte solution. The repeated volume fluctuations cause serious pulverization of the active material and a subsequent loss of contact with the current collector. The CEI continuously breaks and grows, further insulating the surface. Ultimately, the electrode fails after only a few cycles.

1.3 Literature review

To date, there have been many attempts to overcome the challenges associated with the poor cyclability of FeS$_2$ electrodes. Both kinetic and thermodynamic factors limit the reversibility. Several factors influence the stability of pure FeS$_2$ during cycling, the most significant of
which are the source (the naturally formed mineral can be ground into a powder, or material can be
synthesized in a lab) and the crystal size (nanomaterials resist pulverization due to their small starting
size).\textsuperscript{14,26,42,56-59} Often, natural FeS\textsubscript{2} has many defects (such as stacking faults)\textsuperscript{61} and sulfur deficiencies
that have detrimental effects on performance.\textsuperscript{52} Synthetic FeS\textsubscript{2}, conversely, is produced under well
controlled reaction conditions and thus has a better morphology.\textsuperscript{26,55} In 2013, Yersak \textit{et al.}\textsuperscript{26,42}
demonstrated for the first time that synthetic FeS\textsubscript{2} microcrystals (~2.5 \(\mu\)m) could be charged and
discharged at full capacity (four Li-ions per FeS\textsubscript{2} unit) for 20 cycles at an ambient temperature of 60 \(^\circ\)C,
indicating that even at larger sizes, synthetic crystals are superior for battery applications. In 2002, Shao-
Horn \textit{et al.}\textsuperscript{26} demonstrated that natural FeS\textsubscript{2} nanocrystals (NCs, ~50 nm) were superior to microcrystals
(~10 \(\mu\)m) in battery reaction kinetics. As observed for other electrode materials,\textsuperscript{26,56-59} nanostructures can
reduce the ion/electron diffusion distance, increase the electrode/electrolyte contact area,\textsuperscript{26,56-59} and
enhance the accommodation of volume fluctuations.\textsuperscript{56} Moreover, in a lab different nanostructures can be
achieved. Recently, Li \textit{et al.}\textsuperscript{55} prepared highly crystalline FeS\textsubscript{2} nanowires (~15 to 200 nm) by performing
sulfidation of \(\alpha\)-FeF\textsubscript{3}\cdot3H\textsubscript{2}O. Unique synthesis methods such as this enable shape and size control that is
unlikely to be found in nature. Together, these studies imply that synthetic nanocrystals may be
promising for use in LIBs.

\subsection*{1.3.1 Synthetic methods}

Despite the numerous reports the battery performance, most FeS\textsubscript{2} cathodes in the literature are
prepared from micrometer-sized natural\textsuperscript{14,15,21,26,63-65} or synthetic\textsuperscript{14,26,42} FeS\textsubscript{2} particles. Few studies exist on
synthetic, nanostructured FeS\textsubscript{2}.\textsuperscript{55,66} Colloidal FeS\textsubscript{2} nanocrystals, or FeS\textsubscript{2} NC inks,\textsuperscript{42} are desirable for their
compatibility with large scale manufacturing processes, such as roll-to-roll deposition and ink-jet
printing,\textsuperscript{67-69} yet are a challenge to produce. Three wet-chemistry methods for synthesizing FeS\textsubscript{2} NC inks
have been explored, and are summarized in Table 1.1: 1) hot injection (injecting one or all precursors into
a pre-heated flask under a water-free and air-free environment),\textsuperscript{33,34,61,70-78} 2) microwave (heating the
reaction flask with microwave power),\textsuperscript{42,79-81} and 3) solvothermal (heating a sealed reaction vessel in a
furnace or oven).\textsuperscript{82-85} Among the reported results, the hot injection method has been the most widely
successful technique to produce well dispersed, nanocrystalline FeS\textsubscript{2} inks.\textsuperscript{61,62,67,70,72-77,86-88} In 2011,
Puthussery \textit{et al.} pioneered a method for the synthesis of highly-dispersed, spherical FeS\textsubscript{2} NCs (~12 nm in
diameter) that were passivated by octadecylamine;\textsuperscript{57} their work subsequently motivated a series of
publications in protocol modification.\textsuperscript{61,70,72,74,77,87} Some reports in the literature were additionally able to
achieve some degree of shape control. For instance, Gong \textit{et al.} synthesized nanocubes and nanosheets
by tuning the injection temperature;\textsuperscript{70} Lucas \textit{et al.} obtained 80-nm nanocubes by adding
hexadecanesulfonate as the ligand,\textsuperscript{61} and Bai \textit{et al.} produced nanospheres, nanowires, and nanosheets by
varying reaction durations and the molar ratios of reactants.\textsuperscript{77}

Clearly the hot-injection method is widely utilized. However, hot injection requires stringent air-free conditions, which can be labor intensive and may increase the cost of materials synthesis and limit the scalability of the process. For these reasons, several procedures have been developed for the synthesis of FeS\textsubscript{2} NCs using microwave and solvothermal methods.\textsuperscript{42,80-82,84,85,89} These methods have the advantages of being easy to setup and often air-compatible, as all the precursors must be added prior to heating. For example, Li et al.\textsuperscript{81} employed microwave-assisted methods for the synthesis of FeS\textsubscript{2} microspherolites in the size range of 0.6 – 4 \textmu m. Kim et al.\textsuperscript{89} also established a microwave route for polycrystalline FeS\textsubscript{2} aggregates. Wang et al.\textsuperscript{80} synthesized microcubes and microoctahedra by adjusting the pH of the solution using NaOH, and utilizing PVP and the non-ionic surfactant Triton X-100 as ligands. E’jazi et al.\textsuperscript{85} reported an extensive study in 2011 on the effects of raw materials (iron source, sulfur source, and solvent identity), temperature, and molar ratio of materials on the resulting crystal structure and morphology.

| Table 1.1 Reported wet-chemistry methods for the synthesis FeS\textsubscript{2} NCs* |
|-----------------|------|--------|-------|-------|-------|-------|-------|--------|
| Method          | Ref. | Precursor | T/°C  | Solvents | Ligands | Size/nm | Shape   | Ink?   | Air?   |
| Hot Injection   | 67,66| FeCl\textsubscript{2} + 6S | 220   | ODA + DPE | ODA   | 12      | spherical | Yes | No   |
|                 | 70,73| FeCl\textsubscript{2} + 8S | 120 - 220 | ODA + DPE | ODA   | 40 - 80 | cubes     | Yes | No   |
|                 | 72,73| FeCl\textsubscript{2} + 6S | 220   | OLA + TOPO | TOPO   | 60 - 200 | cubes     | Yes | No   |
|                 | 74   | FeCl\textsubscript{2} + 6S | 200 - 250 | HDA + OLA | HDA + OLA | 30 - 50 | cubes     | Yes | No   |
|                 | 75   | FeCl\textsubscript{2} + 6S | 220   | OLA | OLA | 150, 10 | cubes, dendrites | Yes | No   |
|                 | 76   | FeCl\textsubscript{2} + 12S | 240   | ODE | OLA, OLA | 12 - 18 | cubes     | Yes | No   |
|                 | 61   | FeCl\textsubscript{3} + 6S | 220   | OLA | HDSA | 80 | spheres   | No   | Yes |
|                 | 77   | FeCl\textsubscript{2} + 4.5Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} | 139   | DMSO + H\textsubscript{2}O | TGA | 2 - 5, 80 - 120, 100 - 200 | spheres, wires, sheets | Yes | No   |
| Microwave       | 88   | FeZ\textsubscript{3} | 200   | H\textsubscript{2}O | CTAB | 200 | polyhedra | No   | Yes |
|                 | 89   | FeCl\textsubscript{3} + NaHS | N/A   | H\textsubscript{2}O | No | ≥ 100 | spherical | No   | Yes |
|                 | 42   | FeCl\textsubscript{3} + 9S | 190   | H\textsubscript{2}O | PVP | 2000 - 3000 | cubes     | No   | Yes |
|                 | 81   | FeSO\textsubscript{4} + 2S | 200   | EG | PVP | 2700 | spheres | No   | Yes |
| Solvothermal    | 82   | FeCl\textsubscript{2} + S | 200   | H\textsubscript{2}O | Gelatin | ≥ 500 | polyhedra | No   | Yes |
|                 | 83   | FeE\textsubscript{3} | 180   | H\textsubscript{2}O | No | 500 | cubes | No   | Yes |
|                 | 85   | FeSO\textsubscript{4} + 4Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} | 200 | Ethanol | No | ≥ 200 | irregular | No   | Yes |
|                 | 80   | FeCl\textsubscript{2} + 9S | 180   | EG | TX | 250, 150 | cubes, octahedra | No | Yes |

*ODA: octadecylamine; DPE: diphenyl ether; OLA: oleylamine; TOPO: trietylphosphine oxide; HDA: hexadecylamine; ODE: 1-octadecence; OA: oleic acid; HDSA: 1-hexadecanesulfonic acid; DMSO: dimethyl sulfoxide; TGA: thioglycolic acid; FeZ\textsubscript{3}: iron diethylthiophosphate; CTAB: cetyltrimethylammonium bromide; N/A: not available; EG: ethylene glycol; PVP: polyvinylpyrrolidone; FeE\textsubscript{3}: iron diethylthiocarbamate; TX: Triton X-100
Chen et al.\textsuperscript{83} and Wadia et al.\textsuperscript{88} developed hydrothermal methods using single source molecular precursors, which undergo thermal decomposition in an autoclave reactor, and resulting in cubic FeS\textsubscript{2} powders. Extending the utility of the hydrothermal method, Golsheikh et al.\textsuperscript{82} devised a novel synthesis route for the preparation of uniform distribution of nanoparticles on the surface of the graphene sheets, utilizing glucose as a reducing agent for graphene oxide. However, the resulting NCs from these procedures are either very large, or heavily agglomerated and not suitable to form homogeneous inks. Therefore, new methods for the production of FeS\textsubscript{2} inks using scalable, air-compatible, facile techniques are desirable for future, large-scale manufacturing.

### 1.3.2 Enhancement studies for LIBs

In addition to synthesis parameters, many other strategies have been developed to improve the cyclability of battery materials, including conductive additives,\textsuperscript{7,8,24,66,82,90,91} dopants,\textsuperscript{11} and protective coatings.\textsuperscript{8,37,38,92-94} For FeS\textsubscript{2} in particular, carbon powders yielded only slight improvements in cyclability.\textsuperscript{52,54,55,82,95-97} Montoro et al.\textsuperscript{7} coated the electrode surface with a thin layer of gelatin to protect the electrode from electrolyte attack. Strauss et al.\textsuperscript{9} created a protective layer of Li\textsubscript{2}CO\textsubscript{3} and Li\textsubscript{2}O by over-discharging the cathode, enabling the increase of the charging/discharging rate due to higher conductivity and faster reaction kinetics. To alleviate the loss of electrical contact, Zhang et al. made FeS\textsubscript{2}/polyaniline (a conductive polymer, CP) composites.\textsuperscript{38} However, the CP matrix was unable to accommodate the strain of volume fluctuations and too porous to protect the electrode against electrolyte attack and polysulfide dissolution. Takeuchi et al.\textsuperscript{22} used Li\textsubscript{x}FeS\textsubscript{2} instead of FeS\textsubscript{2} as the initial cathode material, in order to decrease the volume-fluctuation percentage. In each case, small cyclability improvements were attained;\textsuperscript{7,22-24,26} however, the success was limited. Therefore, more work is needed to further advance the performance of FeS\textsubscript{2} cathodes.

### 1.3.3 Hypothesis and strategy

After considering the literature reports, we were motivated to explore a strategy that would address all four challenges for FeS\textsubscript{2} cathodes. We predicted the most promising approach would be conformal encapsulation of synthetic FeS\textsubscript{2} nanocrystals in a resilient carbon (RC) matrix that is electrically and ionically conductive, chemically stable, thermally robust, and mechanically resilient. Figure 1.2 illustrates the advantages of this tactic. The local structure would be FeS\textsubscript{2}@RC core/shell nanoparticles (a). After the initial discharge (step 1), the lithiation products Fe, Li\textsubscript{2}S, and Li\textsubscript{2}S\textsubscript{n} will be confined inside the EC shell (b). The resilient shell will effectively be able to accommodate the volume expansion without cracking. Moreover, the CEI growth would be suppressed due to the lack of direct contact between the electrolyte and the active material, and Li\textsubscript{2}S\textsubscript{n} dissolution would be prevented. The Fe, Li\textsubscript{2}S,
and Li$_2$S$_n$ originating from the same composite particle are still in good contact inside the RC shell, and thus the subsequent delithiation (step 2) would be expected to be complete, forming Li$_{1.2}$FeS$_2$. With repeated cycling (step 3), the RC matrix will be stable, maintaining contact with current collector despite recurring volume fluctuations. With this strategy, the poor electrical conductivity of Li$_2$S would be mitigated through its intimate contact with Fe and the good conductivity of the EC shell. The detrimental side reactions between the electrode material and electrolyte solution, as well as the polysulfide dissolution would be prevented. Additionally, the resilient shell would accommodate the volume fluctuations and inhibit crystal pulverization. Consequently, a highly cyclable FeS$_2$ electrode can be expected.

To investigate this strategy, we needed both synthetic FeS$_2$, as well as a coating material. First, we pursued a facile, air-compatible method for the production of FeS$_2$ inks by adapting a hydrothermal procedure from the literature. After a literature review (see Table 1.1), we hypothesized that the solvothermal synthesis of FeS$_2$ NC inks requires efficient dissolution of the precursors in the chosen solvents, good mass transport (such as mechanical stirring) during the reaction, and the aid of an appropriate stabilizing ligand. We tested this hypothesis (see Chapter 3) by screening four solvents, testing several ligands, and studying both stirred and non-stirred reactions. The as-synthesized NCs are polydisperse FeS$_2$ NCs. After a post-synthesis digestive ripening treatment, monodisperse colloidal FeS$_2$ nanospheres were obtained. Furthermore, density functional theory (DFT) computations provided quantum mechanical insights into the decomposition mechanism of the precursor at the molecular level for the first time.

After exploring synthesis parameters, two carbon-coating precursors were explored: glucose and polyacrylonitrile (PAN). The FeS$_2$@RC composite from glucose (see Chapter 4) was synthesized by dispersing autoclave-synthesized FeS$_2$ nanocrystals in an aqueous glucose solution, polymerizing the glucose in a hydrothermal reactor, and finally heating the polymer/FeS$_2$ composite in a tube furnace at 350 °C to partially carbonize the polymer. The FeS$_2$@RC composite electrodes from PAN (see Chapter 4.7) were fabricated by blade-casting a slurry of FeS$_2$, conductive carbon additives, and PAN in dimethylformamide (DMF). As expected, the FeS$_2$@RC electrodes showed superior cyclability compared with the FeS$_2$ electrodes, that is, 25% versus 1% of retention at the 20$^{th}$ cycle. The enhancement mechanism was revealed using electrochemical analysis, XRD, and SEM.
1.4 Thesis organization

Chapters 3-4 are based on material that has been accepted for publication, in which primary authorship was attained. Only formatting changes have been made, and supporting information for each publication can be found in the appendices of this work. Permission to reprint these publications was granted by all coauthors (see Appendix D). This author’s role in said publications included: significant contributions in designing experiments along with the corresponding author (Dr. Yongan Yang), primary data collection, and a primary role in writing, figure-making, and editing. Other coauthors provided either significant data collection, guidance in experimental design, and/or help in the editing process.

Chapter 5 contains material for future publication, in which this author will be primary author for publication.

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The tools with which a researcher can characterize and evaluate materials are varied. This chapter will give a brief overview of the instrumentation theory used in this work in order to provide a suitable context for the reader. In particular, the techniques for battery analysis are summarized in Section 2.2 with the goal of communicating their conventional use for LIB research and the information that can be gained.

2.1 Materials characterization tools

The initial characterization of our inorganic materials included the crystal structure, bulk composition, and sample morphology. Several commonly available techniques were selected that are useful in determining the physical composition of the as-synthesized product. For the sake of simplicity, figures in this section give examples of previously reported pyrite characterizations.

2.1.1 Crystal structure

X-ray diffraction (XRD) was utilized in our studies to determine the bulk crystal structure of a material. Most often, this technique is used \textit{ex situ}; however, it can be extremely useful \textit{in situ} in some cases to observe changes in crystal structure during a reaction or process (Figure 2.1). Crystalline lattice planes have corresponding peaks at angular positions $(2\theta)$, as determined by Bragg’s law:

$$2d \sin \theta = n\lambda$$

where $d$ is the lattice spacing, $\theta$ is the Bragg angle, and $\lambda$ is the x-ray wavelength. When x-rays reflect, they can interfere with each other constructively or destructively and thus resulting in a signal or not, respectively. Constructive interference occurs when the lattice spacing $(d)$ is equal to an integer, $n$. Equation 2.1 shows that long-range crystallinity is inversely related to the peak width; in other words, large crystals have sharp, narrow peaks whereas small crystals have broad peaks. Following that concept, the average grain size can be estimated using the Scherrer equation (Equation 2.2),

$$D_{\text{grain}} = \frac{0.94 K \lambda}{B \cos \theta}$$

where $B$ is the peak at half the maximum height (in radians) after correcting for the instrumental line broadening as determined by a highly crystalline standard.

Following convention, XRD was widely utilized throughout our studies to determine the bulk crystal phase of our synthesized materials. Since XRD is fundamentally based on ordered, crystalline lattices, it is not useful for amorphous materials. It is thus the most powerful in combination with other
characterization techniques such as Raman spectroscopy. Additionally, XRD is not exceptionally sensitive, requiring a significant amount of sample, and thus may not represent the minor impurities in the samples. We therefore paired this technique with a variety of other characterizations for our materials.

2.1.2 Morphology and chemical composition

Electron microscopy (EM) is a multifaceted tool developed in the early 20th century, first reported in a paper by Max Knoll and Ernst Ruska for which Ruska received a Nobel Prize in 1986. While traditional microscopes utilize visible light to image samples, their resolution is limited to about 300 nm by their wavelength according to the Rayleigh criterion,

$$
\delta = \frac{0.61 \lambda}{\mu \sin \beta}
$$

where $\lambda$ is the wavelength of the light source, $\mu$ is the refractive index of the viewing medium, and $\beta$ is the angle of the lens.

EM takes advantage of the smaller wavelength of electrons versus light to achieve much higher resolutions of less than an angstrom (although EMs today still lack perfect electron lenses and thus aren’t

![Figure 2.1](image-url)  

**Figure 2.1.** Example of FeS$_2$ XRD patterns with a reference stick pattern for FeS$_2$. Reproduced with permission, copyright 2012 American Chemical Society.
wavelength limited). There are two main types of EM: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). While both types rely on an electron beam for visualization, they operate on fundamentally different strategies. SEM uses reflected electrons – either secondary or backscattered – to detect the surface. Because the topography can alter the energies and directions of the electrons, important morphological information can be attained (see Figure 2.2A). Moreover, backscattering SEM can help distinguish atomic differences because more electrons are reflected off higher density atoms. TEM is similar to optical microscopy in that the detector measures electrons that pass through the sample and thus provides two-dimensional images of the sample (Figure 2.2B).

In addition to imaging, electron microscopes are traditionally outfitted with detectors for electron diffraction (ED, for TEMs) and energy dispersive x-ray spectroscopy (EDX, for both TEM and SEM). Selected area electron diffraction gives a mathematical representation of a nanocrystal image, displaying bright spots that are inversely related to the lattice spacings in the crystal (Figure 2.2C). For larger areas containing many particles or polycrystalline particles, electron diffraction displays rings related to the lattice spacings. Additionally, the pattern of the spots gives information on the crystal structure (e.g. face-centered cubic vs. orthorhombic). EDX measures the energies of x-rays that are emitted by elements in the sample. These x-rays’ energies are related precisely to the atomic composition of the sample and enable the determination of an estimated sample composition, producing a spectrum as shown by Figure 2.2D.

Figure 2.2. (A) TEM of colloidal FeS₂ nanoparticles; (B) SEM of FeS₂ nanoflakes and nanorods; (C) EDX of a FeS₂ sample; (D) ED of the sample in A. Reproduced with permission, copyright 2011 American Chemical Society and 2004 Elsevier.
For our materials, both low resolution and high resolution TEM (or HRTEM) microscopy was utilized to gain information on morphology and crystallography of a representative sample of particles. When paired with SEM, a relatively complete picture of our as-synthesized nanocrystals, electrodes, and carbon composites could be achieved. EDX was used to confirm the sulfur to iron ratio was close to 2:1 for our synthesized FeS$_2$. Electron diffraction indicated the lattice spacings in our samples matched literature values, giving further evidence that the crystal phase of individual particles or aggregates matched that of the bulk, as determined by XRD.

2.1.3 Absorption spectroscopy

As shown by EM techniques, a large amount of information can be gained through the use of spectroscopy outside the visible range in the electromagnetic spectrum. We characterized our carbon-coated FeS$_2$ composites using three types of absorption spectroscopy: Fourier transform infrared (FTIR), Raman, and ultraviolet-visible-near infrared (UV-Vis-NIR). When a sample is illuminated by radiation at a discrete frequency, the radiation may be absorbed. FTIR and Raman spectroscopies take advantage of this phenomenon to display peaks at frequencies that are representative of specific vibrations of covalent bonds or groups. UV-Vis-NIR utilizes a broad spectrum incorporating visible light and slightly higher (UV) and lower (NIR) frequencies.

When infrared radiation hits a material, the molecules will absorb the radiation at frequencies that correspond to their vibrational frequencies. These vibrations occur most frequently in organic compounds, whose covalent bonds can stretch and bend. Each molecular compound has a unique spectrum based on its functional groups (Figure 2.3A). For instance, a CH$_2$ group has peaks for symmetric and asymmetric stretching, scissoring, rocking, and wagging (see Figure 2.3B). By convention, FTIR frequencies are presented in wavenumbers (cm$^{-1}$) and has a traditional range of 4000 ~ 400 cm$^{-1}$. The wavenumbers are graphed in reverse order (high to low), due to the inverse relationship between wavenumbers and wavelength (nm). Typically, the peaks seen at high wavenumbers represent stretching modes. These modes require more energy than bending or wagging modes. The fingerprint region, from ~1500 – 400 cm$^{-1}$, is so called because the abundance of specific and reproducible signals leads to distinct patterns for organic molecules.

In some cases, the range for FTIR is extended to ~ 10 cm$^{-1}$, which is termed the far-IR range as related to the standard range, which is specified as mid-IR. This area is lower energy than mid-IR, and is therefore sensitive to different types of molecular movement, such as bond rotation, or heavy-atom bending modes. Far-IR is therefore utilized much less often than mid-IR, usually for the characterization of ceramics and organometallics. Pyrite has a specific signal in far-IR (see Figure 2.3C), but no
signal in mid-IR. Therefore, both ranges were useful in our characterizations; the pyrite signal itself could be confirmed with far-IR, and surface ligands or carbon coatings were examined with mid-IR.

UV-Vis-NIR is typically used in photovoltaic applications to characterize a material’s potential as a solar absorber, including its absorption efficiency. A graph of absorption versus wavelength (Figure 2.3D) allows the determination of the sample’s filtering characteristics, which is related to its color and photovoltaic properties. Moreover, the indirect and direct band gap can be determined. However, since the focus of this work was on battery applications we did not employ this technique widely, instead inspecting the electrochemical properties as described in Section 2.2.

Raman spectroscopy provides complementary information to that of FTIR (Figure 2.3E). Alternatively to analyzing vibrational characteristics, the Raman effect is a result of the inelastic scattering of photons. Typically this is achieved by directing a monochromatic laser toward the sample and filtering the scattered light through a monochromator, which removes elastic scattered radiation.
(called Raleigh scattering, or that with the same energy as the original laser). The remaining signal is shifted either to a higher (anti-Stokes) or lower (Stokes) frequency. This shift is due to the loss or gain in energy of the photon resulting from the change in the rotational or vibrational state of the molecule. Raman is often utilized in the characterization of covalent metal bonds, such as metal oxides and sulfides.\textsuperscript{10} It is more sensitive to impurities than XRD and shows signals for other iron sulfides (i.e. FeS, Fe\textsubscript{3}S\textsubscript{4}, and orthorhombic FeS\textsubscript{2}).\textsuperscript{26,29-32} Therefore we employed this useful tool to confirm XRD results. Moreover, carbonaceous materials display peaks corresponding to carbon sp\textsubscript{3} (D band) and sp\textsubscript{2} (G band) bonds; these peaks were paired with FTIR results to determine the composition of our carbon coatings.

2.2 Battery applications

A significant portion of electrochemistry involves the study of chemical reactions that can produce energy, or the storage and conversion of electrochemical energy.\textsuperscript{33,34} The representative system for this process is the rechargeable battery, with the most successful version being the LIB.

2.2.1 LIB characterizations

Several terms and concepts are important when describing the performance of an LIB: cell voltage (the difference in redox potential between the positive and negative electrodes), cyclability (the ability to be repeatedly charged/discharged without significant loss of charge capacity), specific capacity (the amount of charge supplied per unit of mass), retention ratio (charge capacity in subsequent cycles relative to the initial value), and specific power (the amount of energy per unit of mass).\textsuperscript{35}

An electrochemical system typically consists of either a two-electrode or three-electrode setup. Both contain a working electrode composed of the material to be studied, and a counter electrode to complete the circuit. In a three-electrode cell, an additional reference electrode is present to give a highly reproducible redox couple with which to compare the applied or measured potential. In a two-electrode system, the reference electrode plays both roles. As mentioned previously, a battery is essentially a self-contained electrochemical system containing an anode and a cathode that have a potential difference between them. For LIBs, both electrodes must have the capability of incorporating lithium into their crystal structure at different potentials. For research purposes, we utilized lithium “half cells,” which are assembled using lithium foil as the counter and reference. The two electrodes are separated by a thin layer of polypropylene (the separator) soaked in a lithium-salt electrolyte solution, to enable ionic conductivity but prevent electrical contact (Figure 2.4).\textsuperscript{34} LIB materials are typically characterized as anode or cathode materials. However, the anode and cathode alternate in rechargeable batteries depending on whether the cell is being charged or discharged. In this context, anode and cathode
materials are defined as such during discharge, as the battery would be used to power a device. Some common anode and cathode materials can be seen in Table 2.1 along with their properties. As previously mentioned, the voltage of a cell is determined by the redox potential difference between the anode and cathode, with the cathode possessing a much higher potential.

In addition to redox potentials, appropriate LIB electrode materials must be capable of storing lithium. The general operation of an LIB is as follows: 1) a complete circuit allows the flow of electrons from the anode to the cathode, resulting from the oxidation of lithium atoms; 2) the produced lithium ions flow from the anode to the cathode through the electrolyte solution to balance the charge; 3) the lithium ions are incorporated as the cathode material is reduced. The two general mechanisms for lithium storage are intercalation and conversion (Figure 2.4B). The first consists of a layered crystal structure in which lithium rests between the layers. The second involves a complete phase transition, alloying or reacting with the lithium and resulting in a different crystal structure. The reaction for a conversion material can be generalized as:

\[ MX_n + mLi^+ + me^- \rightleftharpoons nLi_{m/n}X + M \]  \hspace{1cm} (2.4)

where M represents a cation and X represents an anion. For FeS$_2$, this reaction is represented by

\[ \text{FeS}_2 + 2Li^+ + 2e^- \rightarrow Li_2S + Fe \]
**Equation 1.6.** The first proposed conversion materials – transition metal oxides – were reported in 2000 by Tarascon et al. Since then, the list has grown to include metal fluorides, chlorides, sulfides, nitrides, phosphates, and more.  

Intercalation materials can reversibly incorporate and extract lithium between the crystal layers, and thus benefit from long cycle life with little damage. The tradeoff to this reversibility is poor energy density. Meanwhile, conversion materials exhibit high energy densities by reacting with several lithium ions per unit, but the resulting volume fluctuation with cycling causes pulverization of crystalline active material. Nonetheless, conversion materials are considered to be quite promising for the future of LIBs and, as described in Chapter 1, considerable effort is being focused on improving their cyclability.

Several specific techniques for assessing the performance of LIB materials were employed in conjunction with our physical characterizations. The structure/performance relationship was carefully analyzed in each material to gauge the accuracy of our predictions and gain insight into possible future directions. The remainder of this section will describe the four key electrochemical techniques utilized for this work.

### 2.2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical technique that can give information about a material’s electrochemical behavior, that is, reduction and oxidation reactions, their relationship to one another (whether they are reversible), and their activation energies. CV is implemented by scanning consistently through a specified potential range and measuring the resulting current using an instrument called a potentiostat. In a lithium cell, the potential is measure versus the Li$^+$/Li reference electrode, which also functions as the counter electrode in a two-electrode cell. The current produced is related to the amount of active material present on the working electrode, and therefore is often presented as mA mg$^{-1}$.

In our studies, CV was utilized as an initial screening technique. Three cycles were measured, and the peak positions and intensities were examined to gain preliminary information on the electrode performance. For example, **Figure 2.5A** shows the CV of the ideal, reversible redox couple potassium ferrocyanide/ferricyanide, $K_3[Fe(CN)_6] + e^- + K^+ \rightleftharpoons K_4[Fe(CN)_6]$  

As the potential is scanned from positive to negative values, reduction occurs according to the forward reaction of **Equation 2.5**, resulting in a well-resolved cathodic peak ($E_{pc}$). When the scan direction is reversed, oxidation occurs following the reverse reaction with an equally resolved anodic peak ($E_{pa}$).  

The information gained by CV is related to the ratios and positions of these peaks (see **Figure 2.5B**). **Equation 2.6** shows the electrical work done by the system ($w_{el}$) is equal to the transported charge ($Q$) multiplied by the potential difference between the electrodes ($\Delta E$), which is equal to the Gibbs free
energy of the reaction ($\Delta G$) at a constant temperature and pressure:

$$\omega_{el} = Q\Delta E = -nF\Delta E = \Delta G_{T,p}$$

where the number of electrons within the reaction ($n$) times the Faraday constant ($F$) equals $Q$. Consequently the peak position relates to the activation energy of the corresponding reduction/oxidation process. Furthermore, the separation of $E_{pc}$ and $E_{pa}$ relates to the reversibility. In a perfect redox system:

$$|E_{pa} - E_{pc}| = 2.2 \frac{RT}{nF} \frac{56.5}{n} \text{ mV at } 25 \text{ °C}$$

where $R$ is the gas constant and $T$ is the temperature (°C). Additionally, the peak currents will be equal, that is, $i_{pa}/i_{pc} = 1$.

For FeS$_2$, the two lithiation steps outlined in Equations 1.4 and 1.5 occur steps occur at 1.9 and 1.7 V vs. $V_{Li+/Li}$ when at 400-450 °C, but the voltages decrease to 1.8 V and 1.6 V at 90 – 135 °C. This indicates a higher $\Delta G$ at the lower temperatures because more electrical work is required to perform the reactions. Furthermore, at room temperature lithium diffusion in the FeS$_2$ bulk slows and limits the lithiation rate. The resulting excess of lithium at the surface causes Li$_2$S and Fe formation and a corresponding loss of a clear phase change; the reactions merge to the same voltage of ~1.5 V at room temperature. We aim to mitigate this problem through our resilient carbon strategy, as the increased conductivity on the surface paired with the small FeS$_2$ particle size will result in a more reversible behavior.

2.2.3 Cyclability

One very important aspect of battery performance is its ability to charge and discharge repeatedly without losing charge capacity. To assess this capability, lithium half cells are assembled; if the lithium
counter electrode is much larger than the working electrode, one can assume that the current produced is limited by the working electrode reaction. All LIB materials, anodes and cathodes, have a positive potential versus V_{Li^+/Li}. If the active material is not lithiated when synthesized (like FeS_2 as opposed to LiCoO_2) the cell will be discharged first; in other words, the working electrode will be reduced (lithiated) as a negative current is applied. An ideal material will have a narrow potential window at which the reaction occurs, resulting in a plateau (see Figure 2.6A).

Next, the specific capacity, usually expressed in mA·h g^{-1}, can be calculated using the current applied, the time for the discharge, and the mass of active material on the working electrode. By repeating the discharge and charge processes repeatedly, a plot of the specific capacity versus the cycle number can be assembled (Figure 2.6B). As mentioned previously, the desired outcome is a stable capacity with no loss throughout cycling. Furthermore, the discharge capacity should be as similar to the charge capacity as possible. This is quantified by the Coulombic Efficiency (CE), which is the discharge capacity divided by the charge capacity and expressed in percent. The CE is an important indicator for real-world feasibility because the cell is a closed system with a limited amount of lithium.

2.2.4 Rate capability

As denoted by the specific capacity, a cell can supply a certain amount of current as limited by the amount of material present and its ability to incorporate lithium. Thus when a current is applied to a cell, the higher the current the faster the cell will deplete. The applied current is called the C rate, which is typically related to the theoretical capacity. For instance, the theoretical (4 electron) capacity for FeS_2 is 890 mA·h g^{-1}. For 1 g of material the capacity is 890 mA·h. A 1C rate is defined as one discharge (or

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Figure 2.6. (A) Current versus time during cycling; (B) discharge/charge curves produced from the applied constant current in A; (C) plot of specific capacity versus cycle number; (D) plot of rate capability versus cycle number.
charge) in one hour, so 890 mA would be applied. A slower rate of C/10, or 0.1C, would be 89 mA. At a faster rate the discharge/charge processes will be kinetically limited. This effect leads to a loss in capacity with increased rate.\textsuperscript{51} Therefore, a way to characterize a material’s kinetics is to conduct a rate capability study, as shown in Figure 2.6C.

2.2.5 Electronic impedance spectroscopy

When a LIB cell is subjected to a potential sweep, like CV, or a constant current, as in cycling, the electrode is driven out of equilibrium and the signal observed is the electrode’s response to that change. Another method of imposing change on the cell is through the application of a small, alternating signal, or frequency. If the response is measured over a wide frequency range, helpful information can be gained about the kinetics and diffusion at electrode interfaces.\textsuperscript{51}

Electrical resistance is the ability of a part of a circuit to resist the flow of electrical current. A battery can be described by an equivalent circuit, with resistors and capacitors representing different interfaces and elements of the battery (Figure 2.7A). Electrochemical impedance spectroscopy, or EIS, is a type of faradaic impedance measurement, in which the Li\textsuperscript{+/Li} redox couple supplies a reference potential for the working electrode. The two main pieces of information gained from this equivalent circuit is the charge transfer resistance (R\textsubscript{ct}) and the Warburg impedance (Z\textsubscript{w}), which is a measurement of the resistance to mass transfer, or diffusion. The Faradaic impedance (Z\textsubscript{f}) is the sum of R\textsubscript{ct} and Z\textsubscript{w}. These elements can be determined by looking at the shape of the Nyquist plot (Figure 2.7B). The semicircle on the left represents the R\textsubscript{ct}, and the linear increase on the right represents the mass transfer. The larger the semicircle, the higher the impedance. Additionally, a system with fast kinetics will show a small, poorly defined semicircle, indicating a mass transfer limitation. A system with slower kinetics will show a large, well-defined semicircle and is thus kinetically limited at the interface. These two factors are important for understanding the charge and discharge processes occurring in an electrode.\textsuperscript{51}

![Figure 2.7](image)

\textbf{Figure 2.7.} (A) Equivalent circuit of an electrochemical cell. (B) Impedance plot for an electrochemical system. Regions of mass-transfer and kinetic control are found at low and high frequencies, respectively.\textsuperscript{51} Reproduced with permission, copyright 1980 Wiley.
2.3 References


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CHAPTER 3
IRON PYRITE NANOCRYSTAL INKS: SOLVOTHERMAL SYNTHESIS,
DIGESTIVE RIPENING, AND REACTION MECHANISM

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3.1 Abstract

Colloidal iron pyrite nanocrystals (or FeS$_2$ NC inks) are desirable as active materials in lithium ion batteries and photovoltaics, and are particularly suitable for large-scale, roll-to-roll deposition or ink-jet printing. However, to date, FeS$_2$ NC inks have only been synthesized using the hot-injection technique, which requires air-free conditions and may not be desirable at an industrial scale. Here, we report the synthesis of monodisperse, colloidal, spherical, and phase-pure FeS$_2$ NCs of 5.5 ± 0.3 nm in diameter via a scalable solvothermal method using iron diethyldithiocarbamate as the precursor, combined with a post digestive ripening process. The phase purity and crystallinity are determined using X-ray diffraction, transmission electron microscopy, far-infrared spectroscopy, and Raman spectroscopy techniques. Through this study, a hypothesis has been verified that solvothermal syntheses can also produce FeS$_2$ NC inks by incorporating three experimental conditions: high solubility of the precursor, efficient mass transport, and sufficient stabilizing ligands. The addition of ligands and stirring decreased the NC size and led to a narrow size distribution. Moreover, using density functional theory calculations, we have identified an acid-mediated decomposition of the precursor as the initial and critical step in the synthesis of FeS$_2$ from iron diethyldithiocarbamate.

3.2 Introduction

Iron pyrite (FeS$_2$) is a widely studied and utilized functional material, particularly for two energy-related applications: lithium ion batteries$^{1-4}$ and photovoltaics.$^{5-8}$ The battery application is based on its activity of electrochemical lithiation.$^{2,9,10}$ Since the 1980s, FeS$_2$ has been utilized as a cathode material in batteries, including rechargeable (secondary) lithium ion batteries at high temperatures (400 °C) and non-
rechargeable (primary) lithium batteries at ambient temperatures (−40 to 60 °C). The photovoltaic application of FeS$_2$ is due to its semiconductor properties, particularly because its band gap ($E_g$) of 0.95 eV is in the ideal range for single-junction photovoltaic devices. Other properties, such as non-toxicity, environmental benignity, cost-effectiveness, and the natural abundance of iron and sulfur, make FeS$_2$ very attractive in the endeavor of establishing a clean and renewable energy-based society.

The promise of using synthetic FeS$_2$ nanostructures in these two applications has intensified in the past decade. In 2002, Shao-Horn et al. reported that natural FeS$_2$ nanocrystals (NCs, ~50 nm) were superior to microcrystals (~10 µm) in battery reaction kinetics. In 2013, Yersak et al. demonstrated for the first time that synthetic FeS$_2$ (~2.5 µm crystals) could be charged and discharged at full capacity (four Li-ions per FeS$_2$ unit) for at least 20 cycles, though at 60 °C. These studies imply that synthetic FeS$_2$ NCs might present enhanced cathode performance, as observed with many other electrode materials.

To be compatible with the large-scale electrode fabrication processes, such as roll-to-roll deposition and ink-jet printing, colloidal NC solutions (NC inks) are highly desirable. Similarly, FeS$_2$ NC inks for photovoltaics have also been a hot topic in recent years. Table 1 summarizes three wet-chemistry methods that have been explored for synthesizing FeS$_2$ NC inks: 1) hot injection (injecting one or all precursors into a pre-heated flask under a water-free and air-free environment); 2) microwave (heating the reaction flask with microwave power); and 3) solvothermal (heating a sealed autoclave vessel in a furnace or oven). Among these strategies, hot-injection is the only successful technique. In 2011, Puthussery et al. pioneered a method for the synthesis of highly-dispersed, spherical FeS$_2$ NCs (~12 nm in diameter) that were passivated by octadecylamine; their work subsequently motivated a series of publications in protocol modification. Some protocols succeeded in synthesizing non-spherical NCs. For instance, Gong et al. synthesized nanocubes and nanosheets by tuning the injection temperature; Lucas et al. obtained 80-nm nanocubes by adding hexadecanesulfonate as the ligand; and Bai et al. produced nanospheres, nanowires, and nanosheets by varying reaction durations and the molar ratios of reactants.

As shown in Table 3.1, this hot-injection method is widespread. However, hot injection requires stringent air-free conditions, which may increase the cost of materials synthesis and limit the scalability of the process. In addition, while FeS$_2$ NCs have been synthesized many times in air-compatible microwave and solvothermal reactors (Table 3.1), the resulting NCs are heavily agglomerated and not suitable to form homogeneous inks. This motivated us to examine if and how one could succeed in synthesizing high-quality FeS$_2$ NC inks using the air-compatible solvothermal technique. After a literature review, we hypothesized that the solvothermal synthesis of FeS$_2$ NC inks requires efficient dissolution of the precursors in the chosen solvents, good mass transport (such as
mechanical stirring) during the reaction, and the aid of an appropriate stabilizing ligand.

This article has tested this hypothesis by screening four solvents, testing several ligands, and studying both stirred and non-stirred reactions. The as-synthesized NCs are polydisperse FeS₂ NCs. After a post-synthesis digestive ripening treatment, monodisperse colloidal FeS₂ nanospheres are obtained. Furthermore, density functional theory (DFT) computations provide quantum mechanical insights into the decomposition mechanism of the precursor at the molecular level for the first time.

3.3 Materials and methods

3.3.1 Chemicals

All chemicals were used as received. Iron chloride hexahydrate (FeCl₃·6H₂O, ACS grade) and polyvinylpyrrolidone (PVP, avg MW 58,000) were purchased from Alfa Aesar. Sodium diethyldithiocarbamate trihydrate (denoted as NaE·3H₂O, E = -S₂CN(CH₂CH₃)₂, >99.0%), octadecylamine (ODA, 97.0%), dodecylamine (DDA, %), oleylamine (OLA, technical grade, 70%),
triphenylphosphine oxide (TOPO, technical grade, 90%), dodecanethiol (DDT, >90%) and sulfur (99.998%) were purchased from Sigma Aldrich. Methanol (ACS grade, Pharmco), ethanol (ACS grade, Pharmco), dimethyl formamide (DMF, 99.8%, Macron), chloroform (CHCl$_3$, ChromAR grade, Macron), and carbon disulfide (CS$_2$, 99.95%) were purchased from Fisher. Toluene (99.5%) and acetone (99.9%) were purchased from VWR. Octadecylxanthate (ODX) was synthesized by following a literature method.

The nanopure water (18.3 MW cm$^{-1}$) was from a Barnstead water purification system.

3.3.2 Preparation of the Iron Diethyldithiocarbamate (FeE$_3$) Precursor

The procedure is a modified version of a method reported in the literature. First, two stock solutions were prepared by dissolving 1 mmol of FeCl$_3$·6H$_2$O in 40 mL of methanol and 3 mmol of NaE·3H$_2$O in 10 mL of methanol. Then the NaE solution was added drop-by-drop to the stirred solution of FeCl$_3$, producing a black precipitate. The obtained product was filtered with a Buchner funnel and washed once with water and three times with methanol. Finally, the collected crystalline powder was dried in a desiccator at room temperature overnight. The typical yield of FeE$_3$ was 400-500 mg.

3.3.3 Solvothermal Synthesis of Iron Pyrite (FeS$_2$) NCs

In a typical synthesis, 0.2 mmol (100 mg) of FeE$_3$, 2 mmol (0.5 M) of ligand, 1.2 mmol (38 mg) of sulfur powder (FeE$_3$:S ratio of 1:6, denoted as 6S), and 4 mL of DMF were added, along with a magnetic stir bar, to a Teflon-lined, stainless steel autoclave (Parr Instr., model 4749, 23 mL capacity). The reactor was sealed and heated at 190 °C for 3 – 22 h in a sand bath set on a stir plate (700 rpm). Finally, the reactor was allowed to cool to room temperature; the resulting product solution was a viscous, dark solution. For more detailed procedures involving other solvents, ligands, ligand concentrations, and non-stirred reactions, please refer to Appendix A.

The resulting product was separated and purified via typical precipitation protocols. First, the crystals and excess ligand were separated using a relative centrifugal force (RCF) of 1228 G (3100 rpm on a RCF-fixed Medilite centrifuge) for five minutes. The supernatant was decanted and the large pellet was dissolved in chloroform. Second, the NCs were precipitated out with acetone (5:1 acetone to CHCl$_3$) and left undisturbed for 12 h; this sedimentation process was repeated three to four times. Third, carbon disulfide was used (5:1 CS$_2$ to CHCl$_3$) to wash away any unreacted sulfur. Finally, the purified NCs were obtained as a colloidal solution in chloroform, after dispersing the collected NCs in chloroform with sonicatation and further removing all aggregates through a gentle centrifugation at RCF = 9 G (200 rpm on Fisher Scientific Marathon 22KBR centrifuge). The critical steps in this protocol were the undisturbed sedimentation and the low-force centrifugation, as higher speed centrifugation steps aggregated the crystals irreversibly.
3.3.4 Digestive Ripening of the Solvothermally-Synthesized FeS₂ NCs

The digestive ripening treatment is a widely used technique for producing monodisperse nanoparticles of metals and metal alloys through refluxing a solution of the premade polydisperse particles with an excess amount of ligands.⁴⁹-⁵⁴ The typical procedure for inducing digestive ripening of FeS₂ in this work was as follows. First, 50 mL of DMF solution containing 0.9 mmol (29 mg) of sulfur powder and 0.01 - 0.75 M of DDA solution was brought to a reflux (~150 °C) in air. Next, a DMF solution containing ~18 mg of FeS₂ (as determined by the theoretical yield) from a typical DMF reaction system was injected into the refluxing system and further heated for 23 h. After cooling naturally to room temperature, the products were extracted for further analysis.

3.3.5 Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a Philips X'Pert X-ray diffractometer with Cu Kα radiation (λ = 0.154054 nm). The XRD samples were prepared by drop-casting the FeS₂ inks onto glass slides to form thin films. Scanning electron microscopy (SEM) images were acquired in a field emission SEM (JEOL JSM-7000F FESEM). The SEM samples were prepared by drop-casting the FeS₂ inks onto silicon wafers to form thin films. Transmission electron microscopy (TEM) images were obtained using a FEI Titan S/TEM operated at 300 kV (in the main text) and a Philips CM200 TEM (in the Supporting Information), equipped with a Princeton Gamma-Tech Prism energy dispersive X-ray spectrometer (EDX). The TEM samples were prepared by dipping ultrathin carbon-coated copper grids (Ted Pella 01824) in FeS₂ reaction solutions and then drying under vacuum (20 mTorr) in a tube furnace at 100 °C for 15 minutes. Fourier transform infrared (FTIR) spectra in the far-IR range were measured using the attenuated total reflection (ATR) mode on powder samples with a Thermo Scientific Nicolet iS50 spectrometer at a spectral resolution of 4 cm⁻¹. UV-visible near infrared absorption (UV-Vis-NIR) spectra were collected on a single-beam spectrometer (Varian Cary 5G) at a spectral resolution of 1 nm. These samples were chloroform solutions in quartz cuvettes. Raman spectra were collected using a WiTec confocal Raman spectrometer (Ar⁺ laser, λ = 532 nm) at a spectral resolution of 5 cm⁻¹. The Raman samples were prepared by pressing FeS₂ NCs (5 wt%) with KBr powders (95 wt%), in order to avoid laser burning. The sizes and size distributions of the synthesized NCs in the TEM images were analyzed using ImageJ (National Institute of Health, version 1.45s).⁵⁵ The NC diameters were calculated from their two-dimensional projections.

3.3.6 Computations

The charge density was calculated using Amsterdam density functional release 2013.01.⁵⁶,⁵⁷ The reported results were computed using a TZ2P basis set⁵⁸ and local density approximation (LDA)
The topology of the charge density was analyzed using Quantum Theory of Atoms in Molecules (QTAIM).  

3.4 Results and discussion  

3.4.1 Solvothermal Synthesis of FeS$_2$ NCs  

The effect of precursor solubility: Following the existing protocol for synthesizing FeS$_2$ using FeE$_3$ through the hydrothermal method, a water suspension of the FeE$_3$ precursor was heated in an autoclave reactor at 180 °C for 18 h, resulting in a mixture of cubes (200 – 1000 nm) and irregular shapes (Figure 3.1A). These results are comparable with the previously reported results. To test our hypothesis that efficient dissolution of FeE$_3$ is necessary to make smaller, well-dispersed NCs, we examined three organic solvents – ODA, toluene, and DMF (Figure A.1-3). It was found that excess sulfur was necessary in all organic solvents to form phase-pure FeS$_2$ and avoid impurities (Figure A.1-3). The best solvent for NC synthesis was DMF (at 190 °C and for 22 h); the results are shown in Figure 3.1B-D. The low magnification TEM image in Figure 3.1B shows large spherical crystals of 350 ± 110 nm in diameter, while the high-resolution TEM (HRTEM) image in Figure 3.1C reveals that the large crystals are actually aggregates of smaller (~ 10 nm) crystals. The selected area electron diffraction pattern with

Figure 3.1. Characterization of the products obtained using water (A and D) and DMF (B-D) as the solvent. (A) SEM image; (B) TEM image and the selected area electron diffraction pattern of the crystals (inset); (C) HRTEM image of one crystal in (B), with arrows indicating grain boundaries; and (D) XRD profiles of the products from water (red) and DMF (blue), with stick patterns denoting the FeS$_2$ reference (JCPDS 01-071-0053).
ring features (the inset in Figure 3.1B) matches the lattice spacings for FeS$_2$ (JCPDS 01-071-0053) and reveals that the particle examined is polycrystalline. The XRD spectra in Figure 3.1D indicate that the products from both water and DMF are phase-pure face-centered cubic (fcc) FeS$_2$. The XRD peaks obtained for the DMF product are broader due to smaller crystal sizes, as expected. However, while the crystal size is smaller, the DMF mediated synthesis of FeS$_2$ did not yield highly dispersed NCs. In the following sections, we will demonstrate two other factors that influence crystal dispersity.

The effects of mass transport and ligand concentration: Two additional factors were hypothesized to be critical for producing highly dispersed NC inks: efficient mass transport during the reaction and ligand concentration. Efficient mass transport is necessary to promote a homogenous distribution of precursors and thus facilitate simultaneous nucleation of particles across the solution followed by growth at nearly the same rate. Since aggregation of NCs is driven by the need to minimize the total surface energy, adsorption of ligands on NC surfaces can lower their total free energies and hence stabilize their sizes. Therefore, ligands are important to prevent aggregation. Ligands and efficient mass transport (such as mechanical stirring) have been widely used in the hot-injection method. However, in all the literature on solvothermal synthesis of FeS$_2$, the autoclave vessels were not stirred, due to the limitations of the heating style in either an oven or a muffle furnace. To overcome this limitation, we replaced the muffle furnace with a sand bath, which allowed for the reaction system to be stirred. ODA was used as the ligand, since it as a solvent produced phase-pure FeS$_2$ and was widely used in the hot injection technique for producing FeS$_2$ NC inks.

The optimal conditions were found to be 0.5 M ODA and stirring for 22 h, resulting in FeS$_2$ NC inks (8 ± 2 nm) (Figure 3.2A) with noticeable spacing between the crystals (inset). When the reaction duration was decreased to 3 h, although highly dispersed NCs (6 ± 1.2 nm) were observed (Figure 3.2B), many small aggregates were also evident (inset). The better dispersion resulting from a longer reaction duration could be due to improved ODA passivation of the NCs during growth. If the reaction system was not stirred (Figure 3.2C), a mixture of colloidal NCs (5.4 ± 1 nm, indicated by arrows), larger crystals (11 ± 9 nm), and aggregates (276 ± 83 nm, not shown here) were obtained. If the ODA concentration was further reduced to 0.1 M (Figure 3.2D), the obtained crystals were similar to those synthesized without ODA (Figure 3.1B), although the aggregates are significantly smaller (120 ± 30 nm in diameter). Stirring the reaction mixture containing 0.1 M ODA resulted in a mixture of dispersed crystals (6.4 ± 1 nm) and aggregates (Figure A.4). For these three experiments (Figure 3.2B-D), all other parameters (temperature, reaction time, and precursor concentration) are the same. Thus, Figure 3.2C and 2D indicate that ligand concentration and stirring are both important for producing FeS$_2$ NC inks. To understand the effect of ligand identity, other ligands were also studied, including ODX, DDA,
OLA, and TOPO; none were found to produce well-dispersed NCs and some failed entirely to form phase-pure FeS$_2$ (Figure A.5). The results in Figure 3.1 and 3.2 together verify our hypothesis that efficient mass transport and surface passivation, which are missing in hydrothermal methods, are necessary for the synthesis of FeS$_2$ NC inks.

### 3.4.2 Comprehensive Characterization

Next, the obtained FeS$_2$ NC inks were systematically characterized. The TEM image in Figure 3.3A was obtained at a higher magnification than that in Figure 3.2D allowing us to visualize the crystal shapes more clearly and to measure the crystal sizes more accurately. Despite the variation in shapes (from sphere-like to rod-like), all the particles are of similar sizes (7.4 ± 1.4 nm), as shown by the histogram of size distribution in Figure 3.3B. The XRD profile in Figure 3.3C confirms the phase purity of face-centered cubic (fcc) FeS$_2$. The representative HRTEM image in Figure 3.3D shows highly resolved lattices of a single-crystalline FeS$_2$ crystal. Lattice modeling with the Crystal Maker® software indicated that the image was taken along the [111] zone axis from the rows of iron atoms, with lattice spacings of 0.42 nm and 0.24 nm from the (011) and (211) planes, respectively. The sulfur atoms (S$_2^-$ pairs) were not observed, likely due to the limited resolution of the TEM used and their low contrast on a carbon film, resulting from sulfur’s low atomic number compared with that of iron.

Figure 3.4 shows the characterization results from EDX, Far-IR, Raman, and UV-Vis-NIR. The
molar ratio of S/Fe extracted from the EDX spectrum (Figure 3.4A and Table 3.2) is 2.08, reasonably consistent with the expected stoichiometry. The C signal can be assigned to the carbon film on the grid as well as the ligands. The O and Cu signals are ascribed to the surface-oxidized copper grid. The Far-IR spectrum (Figure 3.4B) of the FeS\textsubscript{2} NC ink shows three characteristic absorption peaks at 404 cm\textsuperscript{-1}, 344 cm\textsuperscript{-1}, and 286 cm\textsuperscript{-1}, consistent with the values reported in the literature. As expected, the comparison spectrum of FeS\textsubscript{2} mineral also shows three peaks around those positions. However, another peak at 438 cm\textsuperscript{-1} was additionally observed for the mineral. This fourth peak is likely due to the larger crystal size, as observed for the annealed FeS\textsubscript{2} NCs in the literature. Surprisingly, all absorption peaks in the mineral sample were abnormally negative. In addition, TOPO-passivated NCs and ligand-free NCs also showed positive

| Table 3.2. Elemental analysis from EDX spectrum when different peaks are included. |
|-----------------|--------|-------|------|--------|
| Element         | Carbon | Oxygen | Iron | Sulfur |
| Atomic %        |        |        |      |        |
| Atomic %        |        |        |      |        |
| Atomic %        |        |        |      |        |
absorption peaks and negative peaks, respectively (Figure A.6). Hence, it was inferred that the unusually negative absorption peaks are likely a consequence of changes in surface properties. Further elucidation was beyond the scope of this article and is currently under investigation.

The Raman spectra of the FeS$_2$ NCs (red) and mineral (blue) in Figure 3.4C is consistent with literature results.\textsuperscript{67,68} Such shifts in nanomaterials versus the bulk counterparts have been widely reported.\textsuperscript{66,69,70} The peaks centered at 344 cm$^{-1}$, 385 cm$^{-1}$, and 424 cm$^{-1}$ are assigned to the e$_g$ (S-S libration), a$_g$ (S-S stretching) and t$_g$ (coupled libration and stretching) modes, respectively.\textsuperscript{67,68} These spectra are substantially different from other Fe-S compounds, such as marcasite, which has the same chemical formula as pyrite but a different crystal structure (orthorhombic vs. cubic for pyrite).\textsuperscript{71-73}

The UV-Vis-NIR spectrum of the FeS$_2$ NC inks (Figure 3.4D), showing the absorption edge at $\sim$1430 nm and a shoulder peak at $\sim$520 nm, also agrees with the reported values.\textsuperscript{8,35} The optical image in the right side of the inset demonstrates the solubility of the FeS$_2$ NC inks. The left side optical image shows a drop-cast thin film using the obtained FeS$_2$ NC inks, which can be useful for applications in photovoltaics and lithium ion batteries.

3.4.3 Digestive Ripening of the Solvothermally-Synthesized FeS$_2$ NCs

While FeS$_2$ NC inks were successfully synthesized by verifying the hypothesis, our ultimate goal of producing monodisperse (in both size and shape) colloidal FeS$_2$ NCs was not yet achieved. Since the dispersion was moderately improved by extending the reaction duration from 3 h to 22 h, we conducted a post-synthesis digestive ripening to pursue this goal. Digestive ripening is a process to generate
monodisperse NCs from a polydisperse material in the presence of ligands when refluxing the solvent.\textsuperscript{49,54} The mechanism involves the proliferation of small NCs at the cost of dissolving the larger ones,\textsuperscript{51} as opposed to conventional Ostwald ripening, which promotes the growth of large NCs at the expense of smaller ones.\textsuperscript{51}

In an actual synthesis, these two processes are coupled.\textsuperscript{74} The digestive ripening treatment has been previously used for metals,\textsuperscript{50-52,54} alloys,\textsuperscript{49} and metal sulfides,\textsuperscript{75} and was adapted in this work for FeS\textsubscript{2} (Figure A.7-8). Surprisingly, the use of ODA as the ligand in the ripening system resulted in a poorer morphology (Figure A.9). Then, three other ligands were explored – DDT, OLA, and DDA. Interestingly, only DDA produced monodisperse colloidal FeS\textsubscript{2} NCs (Figure 3.5). The monodispersity is demonstrated by a self-assembled monolayer of FeS\textsubscript{2} NCs on the TEM grid (Figure 3.5A) and a 5\% standard deviation in the corresponding size histogram (5.5 ± 0.3 nm). Additional TEM images of

\textbf{Figure 3.5.} Characterization of the digestive ripening product from polydisperse FeS\textsubscript{2} NCs in a refluxing DMF solution with 0.75 M DDA for 23 h. (A) TEM image and (B) histogram showing the size distribution of 100 NCs. (C) XRD spectrum. (D) HRTEM image of an individual FeS\textsubscript{2} nanocrystal, showing lattice fringes that match the (011) and (211) spacings of FeS\textsubscript{2}. 

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different areas are shown in Figure A.10. As in Figure 3.3C and 3D, the XRD data (Figure 3.5C) and HRTEM image (Figure 3.5D) also confirm the phase purity and single-crystallinity of the product.

3.4.4 A Computational Understanding of the Reaction Mechanism

While FeE₃ has been used before to synthesize FeS₂,⁴⁵ the decomposition mechanism of FeE₃ molecules, which is the first and the most critical step for FeS₂ formation, has not been well understood. The structure of the FeE₃ molecule, as shown in Figure 3.6A, is featured with an octahedral coordination of Fe³⁺ surrounded with six sulfur atoms from three E groups, due to the delocalized -CS₂ moieties.⁴⁵ In contrast, in the fcc-structured FeS₂, each Fe²⁺ ion is coordinated with six sulfur atoms and each sulfur atom (in the form of S₂²⁻ pairs) is coordinated with three Fe²⁺ ions and one sulfur atom.⁶⁴,⁶⁵ Thus, two key questions arise. First, how do some of the Fe-S bonds break? Second, how do S₂²⁻ pairs form? The Quantum Theory of Atoms in Molecules (QTAIM), developed by Bader and coworkers,⁷⁶ and extensions of the theory by Knoerr and Eberhart,⁷⁷ were utilized to address these questions. QTAIM is a topological theory that exploits the extrema of the charge density, referred to as critical points or CPs (maxima, minima, and saddle points), to analyze bonding and provide an estimate of structural stability. Ring and bond CPs, both examples of saddle points, are indicated in Figure 3.6 by green and red spheres, respectively.

Our computations suggest an acid-mediated mechanism. Protonation can occur either on the carbon atom or one of the complexed sulfur atoms in the dithiocarbamate moiety (−S₂CNEt₂). As illustrated in Figure 3.6, we propose one possible scenario. First, carbon protonation (Figure 3.6B) weakens both C-S bonds, as shown by the decrease in charge density (Table A.1 and Figure A.11). Second, a nucleophile (HO⁻ or HS⁻) attacks the previously protonated carbamate carbon (the electrophilic center, Figure 3.6C), causing cleavage of the C-S¹ bond. Next, protonation at a sulfur site (S”) results in degradation of the Fe-S” bond, liberating the ligand and producing an Fe₂S¹ intermediate state (Figure 3.6D). Followed by dimerization, as shown in Figure 3.6E, two liberated sulfur atoms are bridged between monomers to form an S-S bond, i.e., the oxidation of S²⁻ to S₂²⁻. It is believed that the protonation, nucleophilic attack, and dimerization would occur at other ligand sites and lead to the ultimate formation of FeS₂ seeds and NCs.

A combination of these two acid catalyzed steps (via protonation of carbon and sulfur in sequence) appears to be responsible for the decomposition of the ligands on the complex. The protonation steps could happen simultaneously or in reverse order. The proton can be from water in the case of a hydrothermal reaction or from H₂S that is produced in situ through the reaction between sulfur and ODA.⁷⁸ While a similar mechanism has been proposed for the hydrothermal synthesis,⁴⁵ our computation
provides, for the first time, quantum mechanically based insight into the reaction mechanism for both hydrothermal and solvothermal reactions. The suggested mechanism may also shed light on the reactions of other metal sulfides from metal diethyldithiocarbamates (ME$_x$)$_{45,79,80}$.

Figure 3.6. The reaction mechanism for the first step of FeS$_2$ formation, proposed by the DFT computation. (A) The left side is the structure of the FeE$_3$ precursor; the right side is a ball-and-stick rendering of the highlighted region shown on the left. The red spheres correspond to bond CPs and the green sphere represents the ring CP for Fe-S-C-S-Fe. (B) Protonation of the central carbon. (C) Nucleophilic attack of the central carbon by HO$^-$ or HS$^-$. (D) Protonation of one of the sulfur atoms in one E moiety. (E) Dimerization through bridging the free sulfurs (circled in red).

3.5 Conclusions

This article reports the synthesis of highly dispersed, colloidal, single-crystalline FeS$_2$ nanocrystals (FeS$_2$ NC inks), which has been a challenge for the hydrothermal technique. Many factors were found to play critical roles, including solvent, precursors, ligand, temperature, time, and stirring. The success was a result of verifying our hypothesis that solvothermal processes can make FeS$_2$ NC inks by using three experimental conditions: high solubility of the precursor, enough stabilizing ligands, and efficient mass transport. The findings here can be applied for synthesizing other types of NC inks. The addition of ligands and stirring decreased the NC size and led to a narrow size distribution. FeS$_2$ NCs directly out of the autoclave reactor were polydisperse, irregular crystals of 7.4 ± 1.4 nm in diameter. A subsequent
digestive-ripening treatment converted them to monodisperse, spherical (5.5 ± 0.3 nm) NCs. These materials can find important applications in lithium ion batteries and photovoltaics, and are suitable for large-scale manufacturing processes. Furthermore, density functional theory computations indicated that the initial and critical step during the solvothermal synthesis was an acid mediated degradation of the precursor, iron diethyldithiocarbamate, gaining quantum mechanical insight into the decomposition mechanism of iron diethyldithiocarbamate at the molecular level for the first time.

3.5.1 Associated content

Additional experimental details, TEM images, XRD profiles, Far-IR spectra of the as-synthesized FeS$_2$ under various conditions, and additional computational details and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors.

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Notes

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CHAPTER 4
RESILIENT CARBON ENCAPSULATION OF IRON PYRITE (FeS$_2$) CATHODES
IN LITHIUM ION BATTERIES

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4.1 Abstract

Converting iron pyrite (FeS$_2$) from a non-cyclable to a cyclable cathode material for lithium ion batteries has been an ongoing challenge in recent years. Herein we report a promising mitigation strategy: wet-chemistry based conformal encapsulation of synthetic FeS$_2$ nanocrystals in a resilient carbon (RC) matrix (FeS$_2$@RC). The FeS$_2$@RC composite was fabricated by dispersing autoclave-synthesized FeS$_2$ nanocrystals in an aqueous glucose solution, polymerizing the glucose in a hydrothermal reactor, and finally heating the polymer/FeS$_2$ composite in a tube furnace to partially carbonize the polymer. The FeS$_2$@RC electrodes showed superior cyclability compared with the FeS$_2$ electrodes, that is, 25% versus 1% of retention at the 20$^{th}$ cycle. Based on electrochemical analysis, XRD study, and SEM characterization, the performance enhancement was attributed to RC’s ability to accommodate volume fluctuation, enhance charge transfer, alleviate detrimental side reactions, and suppress loss of the active material. Furthermore, the remaining issues associated with the current system were identified and future research directions were proposed.

Keywords: carbon encapsulation; iron pyrite, nanocrystals; cathode; lithium ion batteries
4.2 Introduction

Iron pyrite (FeS$_2$) has been extensively studied since the 1980s in battery applications\textsuperscript{1,2} – either as the anode\textsuperscript{3-6} when paired with higher-potential materials (such as LiCoO$_2$) or the cathode when paired with lower-potential materials (such as Li and Na)\textsuperscript{7-12} – due to its high charge capacity, natural abundance, low cost, and non-toxicity.\textsuperscript{2,13} The overall lithiation process was found to consist of two steps:\textsuperscript{14,15}

\[
\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{FeS}_2 \\
\text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Fe}^0 + 2\text{Li}_2\text{S}
\]

Each FeS$_2$ unit accommodates four Li-ions, resulting in a high charge capacity of 890 mA\textperiodcentered h g\textsuperscript{-1}\textsuperscript{2,14,16-18} compared to 372 mA\textperiodcentered h g\textsuperscript{-1} for graphite.\textsuperscript{19} At elevated temperatures (400 – 450 °C), these two steps occur at ~1.9 V and ~1.7 V vs V$_{\text{Li}^+/\text{Li}}$, respectively;\textsuperscript{1,16} both reactions are fully reversible.\textsuperscript{14-18,20} However, when the operating temperature is decreased to room temperature, the phase transition becomes less apparent and the two steps merge to the same voltage of ~1.5 V.\textsuperscript{2,16,21} Additionally, reaction 4.1 cannot be fully reversed due to thermodynamic limitations;\textsuperscript{8,22} instead, only a maximum of 2.8 Li-ions can be extracted out of the cathode. Even worse, fewer and fewer Li-ions are cycled in the subsequent reactions and the electrode fails after a few cycles.\textsuperscript{23}

Four issues have been identified for the poor cyclability of FeS$_2$ cathode.\textsuperscript{2,7,21-26} 1) The lithiation product lithium sulfide (Li$_2$S) presents poor electrical and ionic conductivity (1 x 10$^{-13}$ S cm$^{-1}$).\textsuperscript{23,27} 2) There are complicated detrimental reactions between the electrode material and the electrolyte solution to generate an insulating cathode electrolyte interphase (CEI) on the electrode surface.\textsuperscript{28} 3) The electrical contact between the electrode material and the current collector can be degraded due to volume-fluctuations (up to 260%\textsuperscript{23}) with the lithiation/delithiation cycles. 4) A large amount of electrode material can be lost due to the formation of lithium polysulfides (Li$_2$S$_n$, n $\geq$ 2) that are formed during delithiation processes and highly soluble in electrolyte solutions.\textsuperscript{28-30}

To date, there have been many attempts to overcome these challenges, aiming to cycle 2.8 Li-ions:\textsuperscript{8,23} surface coatings including gelatin\textsuperscript{28} and Li$_2$CO$_3$ \textsuperscript{31}; three-dimensional encapsulation using conductive polymers\textsuperscript{4,32}; conductive additives including carbonaceous materials\textsuperscript{3} and dopants of transitional metals\textsuperscript{33}; and the miniaturization of particle sizes including microcrystals\textsuperscript{2,8-11,29,34,35} and nanocrystals.\textsuperscript{11,36} In addition, prelithiated FeS$_2$ (Li$_x$FeS$_2$) has also been tested.\textsuperscript{23} Despite significant performance improvements, these attempts have not overcome all issues. Therefore, newer strategies are needed.

Learning from other electrode materials,\textsuperscript{11,37-40} we hypothesized that a promising strategy will be to conformally encapsulate synthetic FeS$_2$ nanocrystals in an electrically and ionically conductive, chemically stable, thermally robust, and mechanically resilient carbon (RC) matrix, as shown in Figure 4.1. Nanostructures can reduce the ion/electron diffusion distance, increase the electrode/electrolyte...
contact area, and enhance the accommodation of volume fluctuations. The FeS$_2$@RC core@shell composite (a) is expected to have the following benefits. After the initial lithiation process (step 1), the Fe and Li$_2$S products will be confined inside the RC shell (b), because the resilient shell can effectively accommodate the volume expansion. As a result, the CEI growth due to the direct reaction between the electrode and the electrolyte solution will be effectively suppressed. In the subsequent delithiation process (step 2), a single phase of Li$_x$FeS$_2$ product is expected, since Fe, Li$_2$S, and RC originating from the same composite particle are still in good contact (c). After a number of cycles (step 3), the RC shell will still be stable despite repeated volume fluctuations (d). In this strategy, the poor electrical conductivity of Li$_2$S can be enhanced through its intimate contact with Fe and the good conductivity of the RC shell; the detrimental reactions between the electrode material and the electrolyte will be minimized; the production of polysulfides will be prevented; and the electrode material will not lose its electrical contact with the current collector. Consequently, a FeS$_2$ cathode with high cyclability may be obtained.

This article reports our progress in practicing the aforementioned strategy. The FeS$_2$@RC composite was fabricated by dispersing autoclave-synthesized FeS$_2$ nanocrystals in an aqueous glucose solution, polymerizing the glucose in a hydrothermal reactor, and finally heating the polymer/FeS$_2$ composite in a tube furnace at 350 °C to partially carbonize the polymer. As expected, the FeS$_2$@RC electrodes showed superior cyclability compared with the FeS$_2$ electrodes. The enhancement mechanism was revealed by using electrochemical analysis, XRD, and SEM. Moreover, we have also identified the remaining issues associated with the current system and proposed future research directions.

4.3 Materials and methods

4.3.1 Chemicals and Materials

All chemicals were used as received. Iron (III) chloride hexahydrate (FeCl$_3$●6H$_2$O, ACS grade) and aluminum foil (99.45% trace metals basis, 25 µm) were purchased from Alfa Aesar. Sodium diethyldithiocarbamate (NaE, E = -S$_2$CN(CH$_2$CH$_3$)$_2$, >99.0%), sulfur (99.998%), d-glucose (>99.5%), lithium foil (99.9% trace metals basis, 0.38 mm), bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%), and tetra(ethylene glycol)dimethyl ether (TEGDME, 99%) were purchased from Sigma Aldrich.
Methanol (ACS grade) and ethanol (ACS grade) were purchased from Pharmco. Dimethylformamide (DMF, 99.8%, Macron), chloroform (ChromAR grade, Macron), and carbon disulfide (99.95%) were purchased from Fisher. Acetylene black (35-45 nm), n-methylpyrrolidone (NMP, anhydrous, >99.5%), polyvinylidene fluoride (PVDF, >99.5%), and copper foil (99.99%, 9 µm) were purchased from MTI Corp. The LP40 electrolyte, 1M lithium hexafluorophosphate (LiPF₆) in 50:50 ethylcarbonate/diethylcarbonate (EC/DEC, 0.7ppm H₂O), was purchased from BASF. Nanopure water (18.3 MΩ cm⁻¹) was obtained from a Barnstead water purification system.

4.3.2 Synthesis of FeS₂ nanocrystals

First, the molecular precursor iron (III) diethyldithiocarbamate (denoted as FeE₃) was synthesized from FeCl₃●6H₂O and NaE, following a literature method.³² Then, 0.2 mmol of FeE₃ (100 mg), 2 mmol sulfur powder (32 mg), and 4 mL of DMF were added into a Teflon-lined stainless steel autoclave reactor (Parr Instrument, model 4749). Afterward, the autoclave was heated at 190 °C in a preheated muffle furnace for 3 h. After cooling the reactor to room temperature, the solvent and the dark-grey product were separated via centrifugation at a relative centrifugal force (RCF) of 1228 G (3100 rpm on a RCF-fixed Medilite centrifuge) for five minutes. The collected solid was further washed with a mixture of chloroform and ethanol several times, until the centrifuged supernatant was clear and colorless, followed by one wash with carbon disulfide to remove the unreacted sulfur. Finally, the product was dried in a desiccator at room temperature overnight.

4.3.3 Synthesis of FeS₂@RC Composite (Figure 4.2)

The as-synthesized FeS₂ particles were encapsulated via a hydrothermal polymerization of glucose: 30 mg of premade FeS₂ powder, 0.54 g of glucose, and 3 mL of water were loaded into a stainless steel jar and milled for 30 minutes in a high energy ball mill (SPEX, 8000M). The resulting slurry was fully transferred to an autoclave reactor by washing the milling jar with 3 mL of water, bringing the glucose concentration to 0.5M. The reactor was then autoclaved in a preheated muffle furnace at 160 - 180 °C for 4 - 7 hours. After cooling the autoclave naturally to room temperature, the black product was purified using the above described centrifugation method and thoroughly washed with ethanol and water, before

![Figure 4.2](image-url)  
**Figure 4.2.** Schematic for the synthesis of FeS₂@RC composites using the hydrothermal carbonization of glucose in the presence of pre-made FeS₂, followed by a further dehydration step in a tube furnace.
being dried in a vacuum desiccator overnight. The product at this stage was FeS$_2$ nanoparticles embedded in polymerized glucose. Last, the sample was heated at 350 °C for 4 hours in a tube furnace (MTI Corp, GSL-1100X). The final composite consisted of FeS$_2$ nanoparticles embedded in partially carbonized glucose (resilient carbon), denoted as FeS$_2$@RC. The conversion yield in mass from glucose to RC was determined to be 5.3%. The weight percent of RC in the composite was determined to be 41%, shown in the section of additional experimental details in Appendix B and Figure B.1.

### 4.3.4 Material Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Philips X’Pert X-ray diffractometer using Cu Kα radiation. XRD samples were prepared by dropping acetone suspensions of FeS$_2$ (or FeS$_2$@RC) composites onto glass slides. Scanning electron microscopy (SEM) images were taken on a Field Emission SEM (JEOL JSM-7000F FESEM). Energy Dispersive X-Ray (EDX) spectra were taken on the FESEM using a JEOL EDAX Detecting Unit (JEOL 7000F). Transmission electron microscopy (TEM) images were taken with a Philips CM200 transmission electron microscope. The TEM samples were prepared by dripping ethanol suspensions of the composite onto carbon-coated copper grids (400 mesh, Electron Microscopy Sciences) and then drying in a vacuum desiccator overnight. Fourier transform infrared (FTIR) spectroscopy was taken using the attenuated total reflection (ATR) mode for powder samples on a Thermo Scientific Nicolet iS50 spectrometer at a spectral resolution of 2 cm$^{-1}$. Raman spectroscopy was collected using a WiTec confocal Raman spectrometer (Ar+ laser, λ = 532 nm) at a spectral resolution of 5 cm$^{-1}$. The Raman samples were prepared by mixing FeS$_2$@C (5 wt%) and KBr powders (95 wt%), in order to avoid laser burning.

### 4.3.5 Electrochemical Measurements

The tested electrodes were fabricated using a standard slurry protocol. First, the active materials of FeS$_2$ or FeS$_2$@RC (80 wt%), acetylene black (12 wt%), PVDF binder (8 wt%) were blended with a small amount of NMP in a mortar. Then, the obtained slurry was bladed onto an aluminum foil current collector and dried at 110 °C overnight. Next, the electrodes were punched into small discs of 10 mm in diameter using a compact precision disc cutter (MTI Corp., MSK-T-07). The mass of FeS$_2$ per disc was usually 0.5-1 mg. After that, two-electrode split cells were assembled in an Argon-filled glove box, using the FeS$_2$ (or FeS$_2$@RC) electrode as the working electrode, lithium foil as the anode, and a 25-μm polypropylene membrane (Celgard 2500) as the separator. The assembled cells were taken out of the glove box and quickly sealed with wax to prevent any leakage. Last, the electrode performance was assessed using an 8-channel battery analyzer (MTI Corp., BST8-MA) with standard galvanostatic (constant current) charge/discharge techniques, including the gravimetric charge capacity (Q$_m$) versus...
cycle number, and Coulombic efficiency (CE%), where \( Q_m \) is versus the net mass of FeS\(_2\) and CE% = \( \frac{Q_m}{Q_m, \text{delithiation}} \). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a potentiostat (either a Versastat 4 by Princeton Applied Research or a Reference 600 by Gamry Instruments).

4.4 Results and discussion

4.4.1 Synthesis and characterization of FeS\(_2\) nanocrystals and FeS\(_2\)@RC composite

Previously, glucose has been used as a carbon source to coat a mixture S and FeS\(_2\),\(^3\) where FeS2 particles were larger in the range of 30 – 100 nm, the coating was not conformal, and the carbon layer was only 1- 2 nm. The XRD patterns in Figure 4.3a indicate the acquisition of phase-pure face-centered cubic FeS\(_2\) nanocrystals for both FeS\(_2\) (i) and FeS\(_2\)@RC (ii) samples, according to the standard patterns of FeS\(_2\) (black sticks). The similar average crystal sizes of FeS\(_2\)@RC (13 ± 3 nm) and FeS\(_2\) (14 ± 2 nm), calculated based on the Scherrer equation,\(^44\) imply the effective isolation of FeS\(_2\) nanoparticles by the RC matrix to prevent coalescence during the carbonization process. Coincidently, while the FeS\(_2\) sample is seriously aggregated as shown by the TEM image in Figure 4.3b, the FeS\(_2\)@RC sample in Figure 4.3c-d consists of well-dispersed particles and uniformly coated RC matrix of about 5 nm in thickness. These results confirm the effectiveness of ball-milling in breaking aggregates into individual particles to mix them well with glucose. Initially, we chose 0.5M glucose for 4 hours at 180 °C, according to a literature method used to coat premade Ag nanoparticles.\(^45\) However, these conditions produced very large polymer spheres of ~5 \( \mu \)m in diameter during the hydrothermal polymerization. We hypothesized that the large spheres formed after the initial polymerization on the FeS\(_2\) surface; therefore, shorter reaction times, lower glucose concentrations, and lower reaction temperatures were systematically explored.

![Figure 4.3. Characterization of the as-synthesized FeS\(_2\) nanocrystals and FeS\(_2\)@RC composite. (a) XRD profiles of FeS\(_2\) (i) and FeS\(_2\)@RC (ii). The black sticks denote the patterns of pyrite FeS\(_2\) standard (JCPDS 01-071-0053). (b) TEM image of FeS\(_2\); (c) TEM image of FeS\(_2\)@RC; and (d) Zoom-in of a small area in image (c).](image-url)
A deficient coating was observed when the reaction time was shortened to 2 hours or the glucose concentration was lowered to 0.1 M at 180 °C. The optimal conditions were determined to be 160 °C for 7 h with 0.5 M of glucose, by tuning the reaction time between 4 and 8 h at 160 °C with 0.5 M of glucose: the carbon coating was too thin at 4 hours and excessive polymerization into carbon spheres was observed again at 8 hours.

To understand the nature of the resilient carbon, Fourier Transform Infrared (FTIR) spectroscopy and Raman spectroscopy (Figure 4.4) were employed to characterize both FeS$_2$ and FeS$_2$@RC samples. Pure FeS$_2$ (Figure 4.4a-i) is not active in mid-IR; therefore all labeled peaks in the spectrum of FeS$_2$@RC (Figure 4.4a-ii) must be from the RC matrix and indicate its carbon nature, represented by the strongest peak of C=C, with C-H, C-OH and C=O functional groups. This conclusion is further confirmed by the Raman spectra of FeS$_2$ (Figure 4.4b-i) and FeS$_2$@RC (Figure 4.4b-ii), where the peaks at 343, 380, and 430 cm$^{-1}$ match the literature well for pure FeS$_2$ and the two bands at 1360 and 1566 cm$^{-1}$ are the characteristic D-band and G-band of carbon materials. The broad and overlapped D-band and G-band are characteristic features of RC. These results together confirm the production of the desired FeS$_2$ nanocrystals and FeS$_2$@RC composite.

**4.4.2 Performance assessment of FeS$_2$ and FeS$_2$@RC electrodes**

The cyclic voltammograms of the FeS$_2$ electrodes (Figure 4.5a) revealed a behavior consistent with the literature; between the initial and 20th cycles the lithiation and delithiation peaks were observed to shift from 1.37 V (E$_{Lith}$) and 1.93 V (E$_{Delith}$) to 1.34 V and 2.05 V, respectively. Furthermore, the current intensity decreased dramatically. The lower lithiation potential in the first cycle was assigned to a higher activation energy for fresh FeS$_2$ electrodes. With subsequent cycles, the down-shift of the lithiation peak and the up-shift of the delithiation peak were assigned to the electrochemical irreversibility, due to the deteriorated electrical contact between FeS$_2$ and the current collector. In contrast, the FeS$_2$@RC electrodes show very different behaviors (Figure 4.5b). In the first cycle, the lithiation process showed a shoulder peak at 1.42 V and a broad peak centered at 1.20 V (determined to be from the RC); the
The delithiation peak was at 1.89 V. With cycling, the lithiation and delithiation peaks were consistent at 1.42 V and 1.89 V, respectively; the current intensity did not decrease significantly. Compared with the FeS$_2$ electrodes, these results imply the superior cyclability of the FeS$_2$@RC electrodes. The smaller potential difference of 0.45 V between $E_{\text{Lith}}$ and $E_{\text{Delith}}$ for FeS$_2$@RC, versus 0.52 V for FeS$_2$, indicated better thermodynamic reversibility. The peak at 1.20 V in the first cycle was found to originate from the RC matrix (Figure B.3). In short, the cyclic-voltammetry study implied that the FeS$_2$@RC electrodes would be superior to the FeS$_2$ electrodes.

The subsequent cyclability study (Figure 4.5c) supported the conclusions from cyclic voltammetry. In the initial lithiation process, the FeS$_2$ electrodes obtained a high $Q_m$ of 830 mA$\cdot$h g$^{-1}$, 93% of the theoretical value of 890 mA$\cdot$h g$^{-1}$. After 20 cycles, the FeS$_2$ electrodes exponentially decayed to almost zero. In contrast, the FeS$_2$@RC electrodes showed much better cyclability, though the performance improvement was less than expected, the reasons for which will be analyzed below. The charge capacity was 708 mA$\cdot$h g$^{-1}$ at the first cycle, 130 mA$\cdot$h g$^{-1}$ at the 20th cycle, and 110 mA$\cdot$h g$^{-1}$ at the 50th cycle. Figure 4.5d shows the typical plots of voltage versus $Q_m$ for the FeS$_2$ (○) and FeS$_2$@RC (●) electrodes during both the lithiation (red) and delithiation (black) processes in the first cycle. Two lithiation plateaus at 1.6 V and 1.5 V, observed for the FeS$_2$ electrodes, were consistent with the two-step mechanism reported in the literature.\cite{14,15} The absence of the lithiation plateaus for the FeS$_2$@RC electrodes was most likely due to fast reaction kinetics without an obvious phase transition.\cite{49} The delithiation plateaus for both electrodes were observed at 1.75 V, consistent with the onset voltage of the delithiation peaks in Figure 4.5a and b.\cite{50}

### 4.4.3 Correlation of the structure-performance relationship

First, ex situ XRD was employed to monitor the crystalline phases of FeS$_2$ (Figure 4.6a) and FeS$_2$@RC (Figure 4.6b) electrodes after lithiation/delithiation cycles. As expected, the fresh electrodes (Figure 4.6a-i and Figure 4.6b-i), showed signals only from FeS$_2$ (black) and the Al current collector
(the asterisked peaks). After 0.5 cycle (ii), that is, at the end of the first lithiation, the FeS$_2$ electrodes showed the appearance of Li$_2$S (cyan) and the disappearance of FeS$_2$; however, the FeS$_2$@RC electrodes showed the existence of both Li$_2$S (0) and FeS$_2$ ($\downarrow$). The signals from Fe (■) may be masked by the signals from Al. The observed lithiation process was consistent with the mechanism reported in the literature$^{14,15}$ though some FeS$_2$ nanocrystals in the FeS$_2$@RC electrodes were not accessible. After one cycle (iii), that is, at the end of the first delithiation, strong signals from unreacted Li$_2$S were observed for the FeS$_2$ electrodes; in contrast, no signals from Li$_2$S were observed for the FeS$_2$@RC electrodes. In both cases, the Li$_{1.2}$FeS$_2$ product was believed to be amorphous, referring to the standard patterns (pink) and the literature report.$^2$ After 20 cycles (iv), the FeS$_2$ electrodes were dominated with Li$_2$S; however, the FeS$_2$@RC electrodes showed signals from both Li$_2$S and FeS$_2$. These results indicate that the inferior cyclability of the FeS$_2$ electrodes was strongly correlated to the accumulation of isolated Li$_2$S and that the initial low charge capacity of the FeS$_2$@RC electrodes was due to some FeS$_2$ nanoparticles being inaccessible.

To gain a deeper understanding of the above conclusion, ex situ SEM was employed to observe the morphological changes of the FeS$_2$ and FeS$_2$@RC electrodes with cycling. As shown in Figure 4.6c and Figure 4.6d respectively, the fresh FeS$_2$ and FeS$_2$@RC electrodes had similar morphologies. However, after 20 cycles, the FeS$_2$ electrodes exhibited badly cracked surfaces, as shown in Figure 4.6e and the inset therein; the FeS$_2$@RC electrodes showed homogeneous and crack-free surfaces, as shown in Figure 4.6f and the inset therein. These results indicated that the RC matrix effectively accommodated the volume fluctuation and alleviated the otherwise inevitable damage from CEI growth.

![Figure 4.6](image_url)

**Figure 4.6.** XRD patterns of the (A) FeS$_2$ and (B) FeS$_2$@C electrodes after various cycles. Standard patterns are shown for FeS$_2$ (black – JCPDS 01-071-0053), Li$_2$S (cyan – JCPDS 00-023-0369), and Li$_{1.2}$FeS$_2$ (pink – JCPDS 00-036-1088). Peaks from Fe (■) and the Al substrate (*) are also indicated. (c) and (d): SEM images of the as-fabricated FeS$_2$ and FeS$_2$@RC electrodes, respectively; (e) and (f): SEM images of the electrochemically-cycled (20 cycles) FeS$_2$ and FeS$_2$@RC electrodes, respectively.
Following the *ex situ* studies, electrochemical impedance spectroscopy (EIS) was used to correlate the observations from SEM with the electrochemical performance. The obtained EIS spectra, as shown in Figure 4.8a (FeS$_2$) and Figure 4.8b (FeS$_2$@RC), revealed very different behaviors between these two electrodes. With cycling, the charge transfer resistance ($R_{ct}$, obtained from the extrapolated intercept of the semicircle on the $Z_{Re}$ axis) of the FeS$_2$ electrodes increased constantly for both the lithiated and delithiated states, with a vigorous oscillation between the lithiated (high resistance) and delithiated (low resistance) processes (Figure 4.8a). Moreover, the $R_{ct}$ along with the lithiated process increased more dramatically. These results strongly indicated that the lithiation process damaged the FeS$_2$ electrode more severely than the delithiation process.$^{38}$ Furthermore, the appearance of multiple semicircles with cycling indicated the evolution of multi-step charge-transfer reactions, corroborating the surface cracks observed.

![Figure 4.7](image)

Figure 4.7. (a) Schematic illustration of two types of FeS$_2$@RC nanoparticles with thinner RC shells (1) and thicker RC shells (2). (b) Plots of charge capacity versus cycle number for the control electrodes made of RC instead of FeS$_2$ and FeS$_2$@RC for three conditions using different potential windows and charging rates. (c) The hypothesized mechanism for the charge capacity contributed by the RC matrix due to the oxygen-containing functional groups. (d) The effect of potential window on the charge-capacity retention of FeS$_2$@RC electrodes. (e) The effect of electrolyte solution on the charge-capacity retention of FeS$_2$@RC electrodes. (f) The retention plots of FeS$_2$ and FeS$_2$@RC electrodes shown in Figure 4.6c after correcting the contribution of the RC matrices.
in SEM (Figure 4.6e). On the contrary, while the Rct of the FeS2@RC electrodes started high due to the low conductivity of the RC matrix, the Rct (Figure 4.8b) decreased steadily with cycling, showing no oscillation between the lithiation and delithiation processes. This indicated the continuous improvement rather than the deterioration of the electrical conductivity and electrode/electrolyte interface. These results strongly indicated that the RC matrix suppressed the loss of electrical contact by accommodating the volume fluctuation.

The analysis of Figure 4.5-4.7 allows us to draw several important conclusions. The poor cyclability of the FeS2 electrodes was strongly correlated to the volume-fluctuation induced pulverization of the electrode material, cracks in the surface layer, loss of electrical contacts, and decreased conductivity. The cyclability of the FeS2@RC electrodes was improved by the enhanced accommodation of the volume-fluctuation, due to the RC matrix. However, the charge capacity was lower, mainly due to some FeS2 particles being inaccessible. The CEI was also significantly stabilized by the RC matrix. Furthermore, we hypothesized four factors to interpret the limited performance improvement of the FeS2@RC electrodes: 1) The conductivity of the RC matrix was not high enough, making some FeS2 nanocrystals coated with thick RC shells inaccessible to the electrolyte; 2) The RC matrix contributed substantially to the initial charge capacity; 3) The RC contribution was due to the irreversible consumption of lithium by the oxygen-containing functional groups; 4) The currently used electrolyte solution was not the best system for FeS2, as reported in the literature.

4.4.4 Verification of the hypothesized factors for the limited performance improvement of the FeS2@RC electrodes

The first hypothesis is illustrated in Figure 4.7a, where thinner RC shells (1) encapsulated FeS2 nanocrystals are accessible and thicker RC shells (2) encapsulated FeS2 nanocrystals are inaccessible at the charge rate used in this work. This hypothesis has been verified by the XRD data in Figure 4.5b showing strong signals of unreacted FeS2 even at the end of lithiation. The second hypothesis was proposed on the basis of a significant drop in charge capacity during the second cycle (242 mA•h g⁻¹) from the initial value of 708 mA•h g⁻¹. To verify this, we measured the charge capacity of pure RC powder versus cycle number (Figure 4.7b). The synthesized RC powder showed comparable chemical compositions as the RC in the FeS2@RC composite (Figure B.4). Surprisingly, under the typical conditions of [0.8, 2.2] V and 0.1C (●) used for assessing FeS2@RC electrodes, the initial charge capacity was only 39 mA•h g⁻¹ and then remained constant at ~10 mA•h g⁻¹ in the following cycles. We speculated that this was due to the underestimated charge capacity of the RC matrix, because only a very thin layer of RC matrix can be active at the tested charge/discharge rate. Therefore, to increase the Li-penetration depth in the RC matrix, we lowered the rate to 0.05C (▲). The initial charge capacity was
almost doubled (72 mA•h g⁻¹); however, in subsequent cycles the charge capacity was still ~10 mA•h g⁻¹. Limited by the current range of our battery analyzer, we could not further lower the charge/discharge rate to quantify the maximum contribution of the RC matrix. Nevertheless, considering the facts that the RC shells encapsulating FeS₂ nanocrystals were only a few to tens of nm and the RC particles in the control electrode (as shown by Figure B.2f) were on the order of 5 mm in radius, the theoretical Qₘ,RC could be one order of magnitude higher than the detected value. By assuming Qₘ,RC = 300 mA•h g⁻¹, the corrected Qₘ,FeS₂ in the first cycle would be 486 mA•h g⁻¹ (refer to Appendix B for the calculation details). Since the lithium was captured by the RC matrix mainly in the first cycle and the charge capacity in the subsequent cycles was negligible (Figure 4.7b), the corrected Qₘ,FeS₂ for the 2nd cycle and beyond for the FeS₂@RC electrodes in Figure 4.5c would not be significantly changed. Assuming the Qₘ,RC = 20 mA•h g⁻¹ in the 2nd cycle, the corrected Qₘ,FeS₂ would be 229 mA•h g⁻¹; the corresponding retention percent was calculated to be 47% – consistent with that of FeS₂ electrode.

If the third hypothesis illustrated in Figure 4.7c was correct, we would expect to observe improved cyclability by tuning the potential window. When changing the potential window to [1.1, 2.4] V, we did observe a substantial improvement in the retention (Figure 4.7d). The substantially suppressed Qₘ,RC under this new condition (m, in Figure 4.7b) further corroborated the above judgment. To verify the fourth hypothesis, we changed the electrolyte solution from 1 M LiPF₆ in 50:50 EC/DEC to 1 M LiTFSI in TEGDME and observed the expected performance improvement as shown in Figure 4.7e. After verifying all proposed hypotheses, we graphed the retention plots (Figure 4.7f) of FeS₂ and FeS₂@RC electrodes shown in Figure 4.5c, after correcting the contribution of the RC matrices. As expected, the FeS₂@RC electrodes showed much better cyclability than the FeS₂ electrodes.

4.4.5 Synthesis and characterization of FeS₂ nanocrystals and FeS₂@RC composite

Previously, glucose has been used as a carbon source to coat a mixture S and FeS₂,³ where FeS₂
particles were larger in the range of 30 – 100 nm, the coating was not conformal, and the carbon layer was only 1-2 nm. The XRD patterns in Figure 4.3a indicate the acquisition of phase-pure face-centered cubic FeS$_2$ nanocrystals for both FeS$_2$ (i) and FeS$_2$@RC (ii) samples, according to the standard patterns of FeS$_2$ (black sticks). The similar average crystal sizes of FeS$_2$@RC (13 ± 3 nm) and FeS$_2$ (14 ± 2 nm), calculated based on the Scherrer equation, imply the effective isolation of FeS$_2$ nanoparticles by the RC matrix to prevent coalescence during the carbonization process. Coincidentally, while the FeS$_2$ sample is seriously aggregated as shown by the TEM image in Figure 4.3b, the FeS$_2$@RC sample in Figure 4.3c-d consists of well-dispersed particles and uniformly coated RC matrix of about 5 nm in thickness. These results confirm the effectiveness of ball-milling in breaking aggregates into individual particles to mix them well with glucose. Initially, we chose 0.5M glucose for 4 hours at 180 °C, according to a literature method used to coat premade Ag nanoparticles. However, these conditions produced very large polymer spheres of ~5 mm in diameter during the hydrothermal polymerization. We hypothesized that the large spheres formed after the initial polymerization on the FeS$_2$ surface; therefore shorter reaction times, lower glucose concentrations, and lower reaction temperatures were systematically explored (Figure B.2). A deficient coating was observed when the reaction time was shortened to 2 hours or the glucose concentration was lowered to 0.1 M at 180 °C. The optimal conditions were determined to be 160 °C for 7 h with 0.5 M of glucose, by tuning the reaction time between 4 and 8 h at 160 °C with 0.5 M of glucose: the carbon coating was too thin at 4 hours and excessive polymerization into carbon spheres was observed again at 8 hours.

To understand the nature of the resilient carbon, Fourier Transform Infrared (FTIR) spectroscopy and Raman spectroscopy (Figure 4.4) were employed to characterize both FeS$_2$ and FeS$_2$@RC samples. Pure FeS$_2$ (Figure 4.4a-i) is not active in mid-IR; therefore all labeled peaks in the spectrum of FeS$_2$@RC (Figure 4.4a-ii) must be from the RC matrix and indicate its carbon nature, represented by the strongest peak of C=C, with C-H, C-OH and C=O functional groups. This conclusion is further confirmed by the Raman spectra of FeS$_2$ (Figure 4.4b-i) and FeS$_2$@RC (Figure 4.4b-ii), where the peaks at 343, 380, and 430 cm$^{-1}$ match the literature well for pure FeS$_2$ and the two bands at 1360 and 1566 cm$^{-1}$ are the characteristic D-band and G-band of carbon materials. The broad and overlapped D-band and G-band are characteristic features of RC. These results together confirm the production of the desired FeS$_2$ nanocrystals and FeS$_2$@RC composite.

4.4.6 Performance assessment of FeS$_2$ and FeS$_2$@RC electrodes

The cyclic voltammograms of the FeS$_2$ electrodes (Figure 4.5a) revealed a behavior consistent with the literature; between the initial and 20$^{th}$ cycles the lithiation and delithiation peaks were observed to shift from 1.37 V (E$_{Lith}$) and 1.93 V (E$_{Delith}$) to 1.34 V and 2.05 V, respectively. Furthermore, the current
intensity decreased dramatically. The lower lithiation potential in the first cycle was assigned to a higher activation energy for fresh FeS$_2$ electrodes. With subsequent cycles, the down-shift of the lithiation peak and the up-shift of the delithiation peak were assigned to the electrochemical irreversibility, due to the deteriorated electrical contact between FeS$_2$ and the current collector. In contrast, the FeS$_2$@RC electrodes show very different behaviors (Figure 4.5b). In the first cycle, the lithiation process showed a shoulder peak at 1.42 V and a broad peak centered at 1.20 V (determined to be from the RC); the delithiation peak was at 1.89 V. With cycling, the lithiation and delithiation peaks were consistent at 1.42 V and 1.89 V, respectively; the current intensity did not decrease significantly. Compared with the FeS$_2$ electrodes, these results imply the superior cyclability of the FeS$_2$@RC electrodes. The smaller potential difference of 0.45 V between $E_{\text{Lith}}$ and $E_{\text{Delith}}$ for FeS$_2$@RC, versus 0.52 V for FeS$_2$, indicated better thermodynamic reversibility. The peak at 1.20 V in the first cycle was found to originate from the RC matrix (Figure B.3). In short, the cyclic voltammetry study implied that the FeS$_2$@RC electrodes would be superior to the FeS$_2$ electrodes.

The subsequent cyclability study (Figure 4.5c) supported the conclusions from cyclic voltammetry. In the initial lithiation process, the FeS$_2$ electrodes obtained a high $Q_m$ of 830 mA•h g$^{-1}$, 93% of the theoretical value of 890 mA•h g$^{-1}$. After 20 cycles, the FeS$_2$ electrodes exponentially decayed to almost zero. In contrast, the FeS$_2$@RC electrodes showed much better cyclability, though the performance improvement was less than expected, the reasons for which will be analyzed below. The charge capacity was 708 mA•h g$^{-1}$ at the first cycle, 130 mA•h g$^{-1}$ at the 20$^{th}$ cycle, and 110 mA•h g$^{-1}$ at the 50$^{th}$ cycle. Figure 4.5d shows the typical plots of voltage versus $Q_m$ for the FeS$_2$ (○) and FeS$_2$@RC (●) electrodes during both the lithiation (red) and delithiation (black) processes in the first cycle. Two lithiation plateaus at 1.6 V and 1.5 V, observed for the FeS$_2$ electrodes, were consistent with the two-step mechanism reported in the literature. The absence of the lithiation plateaus for the FeS$_2$@RC electrodes was most likely due to fast reaction kinetics without an obvious phase transition. The delithiation plateaus for both electrodes were observed at 1.75 V, consistent with the onset voltage of the delithiation peaks in Figure 4.5a and b. 50

4.4.7 Correlation of the structure-performance relationship

First, ex situ XRD was employed to monitor the crystalline phases of FeS$_2$ (Figure 4.6a) and FeS$_2$@RC (Figure 4.6b) electrodes after lithiation/delithiation cycles. As expected, the fresh electrodes (Figure 4.6a-i and Figure 4.6b-i), showed signals only from FeS$_2$ (black) and the Al current collector (the asterisked peaks). After 0.5 cycle (ii), that is, at the end of the first lithiation, the FeS$_2$ electrodes showed the appearance of Li$_2$S (cyan) and the disappearance of FeS$_2$; however, the FeS$_2$@RC electrodes showed the existence of both Li$_2$S (0) and FeS$_2$ (↓). The signals from Fe (■) may be masked by the
signals from Al. The observed lithiation process was consistent with the mechanism reported in the literature,\textsuperscript{14,15} though some FeS\textsubscript{2} nanocrystals in the FeS\textsubscript{2}@RC electrodes were not accessible. After one cycle (iii), that is, at the end of the first delithiation, strong signals from unreacted Li\textsubscript{2}S were observed for the FeS\textsubscript{2} electrodes; in contrast, no signals from Li\textsubscript{2}S were observed for the FeS\textsubscript{2}@RC electrodes. In both cases, the Li\textsubscript{1.2}FeS\textsubscript{2} product was believed to be amorphous, referring to the standard patterns (pink) and the literature report.\textsuperscript{2} After 20 cycles (iv), the FeS\textsubscript{2} electrodes were dominated with Li\textsubscript{2}S; however, the FeS\textsubscript{2}@RC electrodes showed signals from both Li\textsubscript{2}S and FeS\textsubscript{2}. These results indicate that the inferior cyclability of the FeS\textsubscript{2} electrodes was strongly correlated to the accumulation of isolated Li\textsubscript{2}S and that the initial low charge capacity of the FeS\textsubscript{2}@RC electrodes was due to some FeS\textsubscript{2} nanoparticles being inaccessible.

To gain a deeper understanding of the above conclusion, \textit{ex situ} SEM was employed to observe the morphological changes of the FeS\textsubscript{2} and FeS\textsubscript{2}@RC electrodes with cycling. As shown in Figure 4.6c and Figure 4.6d respectively, the fresh FeS\textsubscript{2} and FeS\textsubscript{2}@RC electrodes had similar morphologies. However, after 20 cycles, the FeS\textsubscript{2} electrodes exhibited badly cracked surfaces, as shown in Figure 4.6e and the inset therein; the FeS\textsubscript{2}@RC electrodes showed homogeneous and crack-free surfaces, as shown in Figure 4.6f and the inset therein. These results indicated that the RC matrix effectively accommodated the volume fluctuation and alleviated the otherwise inevitable damage from CEI growth.

Following the \textit{ex situ} studies, electrochemical impedance spectroscopy (EIS) was used to correlate the observations from SEM with the electrochemical performance. The obtained EIS spectra, as shown in Figure 4.8a (FeS\textsubscript{2}) and Figure 4.8b (FeS\textsubscript{2}@RC), revealed very different behaviors between these two electrodes. With cycling, the charge transfer resistance (R\textsubscript{ct}, obtained from the extrapolated intercept of the semicircle on the Z\textsubscript{Re} axis) of the FeS\textsubscript{2} electrodes increased constantly for both the lithiated and delithiated states, with a vigorous oscillation between the lithiated (high resistance) and delithiated (low resistance) processes (Figure 4.8a). Moreover, the R\textsubscript{ct} along with the lithiated process increased more dramatically. These results strongly indicated that the lithiation process damaged the FeS\textsubscript{2} electrode more severely than the delithiation process.\textsuperscript{38} Furthermore, the appearance of multiple semicircles with cycling indicated the evolution of multi-step charge-transfer reactions, corroborating the surface cracks observed in SEM (Figure 4.6e). On the contrary, while the R\textsubscript{ct} of the FeS\textsubscript{2}@RC electrodes started high due to the low conductivity of the RC matrix, the R\textsubscript{ct} (Figure 4.8b) decreased steadily with cycling, showing no oscillation between the lithiation and delithiation processes. This indicated the continuous improvement rather than the deterioration of the electrical conductivity and electrode/electrolyte interface.\textsuperscript{38} These results strongly indicated that the RC matrix suppressed the loss of electrical contact by accommodating the volume fluctuation.
The analysis of Figure 4.5-4.7 allows us to draw several important conclusions. The poor cyclability of the FeS$_2$ electrodes was strongly correlated to the volume-fluctuation induced pulverization of the electrode material, cracks in the surface layer, loss of electrical contacts, and decreased conductivity. The cyclability of the FeS$_2$@RC electrodes was improved by the enhanced accommodation of the volume-fluctuation, due to the RC matrix. However, the charge capacity was lower, mainly due to some FeS$_2$ particles being inaccessible. The CEI was also significantly stabilized by the RC matrix. Furthermore, we hypothesized four factors to interpret the limited performance improvement of the FeS$_2$@RC electrodes: 1) The conductivity of the RC matrix was not high enough, making some FeS$_2$ nanocrystals coated with thick RC shells inaccessible to the electrolyte; 2) The RC matrix contributed substantially to the initial charge capacity; 3) The RC contribution was due to the irreversible consumption of lithium by the oxygen-containing functional groups; 4) The currently used electrolyte solution was not the best system for FeS$_2$, as reported in the literature.$^{34,51}$

4.4.8 Verification of the hypothesized factors for the limited performance improvement of the FeS$_2$@RC electrodes

The first hypothesis is illustrated in Figure 4.7a, where thinner RC shells (1) encapsulated FeS$_2$ nanocrystals are accessible and thicker RC shells (2) encapsulated FeS$_2$ nanocrystals are inaccessible at the charge rate used in this work. This hypothesis has been verified by the XRD data in Figure 4.5b showing strong signals of unreacted FeS$_2$ even at the end of lithiation. The second hypothesis was proposed on the basis of a significant drop in charge capacity during the second cycle (242 mA•h g$^{-1}$) from the initial value of 708 mA•h g$^{-1}$. To verify this, we measured the charge capacity of pure RC powder versus cycle number (Figure 4.7b). The synthesized RC powder showed comparable chemical compositions as the RC in the FeS$_2$@RC composite (Figure B.4). Surprisingly, under the typical conditions of [0.8, 2.2] V and 0.1C (●) used for assessing FeS$_2$@RC electrodes, the initial charge capacity was only 39 mA•h g$^{-1}$ and then remained constant at ~10 mA•h g$^{-1}$ in the following cycles. We speculated that this was due to the underestimated charge capacity of the RC matrix, because only a very thin layer of RC matrix can be active at the tested charge/discharge rate. Therefore, to increase the Li-penetration depth in the RC matrix, we lowered the rate to 0.05C (▲). The initial charge capacity was almost doubled (72 mA•h g$^{-1}$); however, in subsequent cycles the charge capacity was still ~10 mA•h g$^{-1}$. Limited by the current range of our battery analyzer, we could not further lower the charge/discharge rate to quantify the maximum contribution of the RC matrix. Nevertheless, considering the facts that the RC shells encapsulating FeS$_2$ nanocrystals were only a few to tens of nm and the RC particles in the control electrode (as shown by Figure B.2f) were on the order of 5 mm in radius, the theoretical $Q_{m,RC}$ could be one order of magnitude higher than the detected value. By assuming $Q_{m,RC} = 300$ mA•h g$^{-1}$, the corrected
Q_{m,FeS_2} in the first cycle would be 486 mA•h g\(^{-1}\) (refer to Appendix B for the calculation details). Since the lithium was captured by the RC matrix mainly in the first cycle and the charge capacity in the subsequent cycles was negligible (Figure 4.7b), the corrected Q_{m,FeS_2} for the 2\(^{nd}\) cycle and beyond for the FeS_2@RC electrodes in Figure 4.5c would not be significantly changed. Assuming the Q_{m,RC} = 20 mA•h g\(^{-1}\) in the 2\(^{nd}\) cycle, the corrected Q_{m,FeS_2} would be 229 mA•h g\(^{-1}\); the corresponding retention percent was calculated to be 47\% – consistent with that of FeS_2 electrode.

If the third hypothesis illustrated in Figure 4.7c was correct, we would expect to observe improved cyclability by tuning the potential window. When changing the potential window to [1.1, 2.4] V, we did observe a substantial improvement in the retention (Figure 4.7d). The substantially suppressed Q_{m,RC} under this new condition (■, in Figure 4.7b) further corroborated the above judgment. To verify the fourth hypothesis, we changed the electrolyte solution from 1 M LiPF_6 in 50:50 EC/DEC to 1 M LiTFSI in TEGDME and observed the expected performance improvement as shown in Figure 4.7e. After verifying all proposed hypotheses, we graphed the retention plots (Figure 4.7f) of FeS_2 and FeS_2@RC electrodes shown in Figure 4.5c, after correcting the contribution of the RC matrices. As expected, the FeS_2@RC electrodes showed much better cyclability than the FeS_2 electrodes.

4.5 Conclusions

In summary, this article has reported a promising strategy to address the challenges that limit the cyclability of FeS_2 cathodes for LIBs: encapsulation of FeS_2 nanocrystals in a resilient carbon (RC) matrix. The FeS_2@RC composite was produced by mixing premade-FeS_2 nanocrystals with glucose, polymerizing glucose in a hydrothermal reactor, and partially carbonizing the resulting polymer in a tube furnace. As expected, the FeS_2@RC electrodes outperformed the FeS_2 electrodes, retaining 25\% capacity at the 20\(^{th}\) cycle versus 1\% for FeS_2. The performance enhancement was ascribed to RC’s effective accommodation of the volume-fluctuations with the lithiation/delithiation cycles, enhancement of the charge transfer across the electrode/electrolyte interface, alleviation of the detrimental reactions at the FeS_2/electrolyte interface, and suppression of the dissolution loss of the active material into the electrolyte solution. The major factors for the rapid failure of FeS_2 electrodes were found to be the poor reversibility of Li_2S, the serious growth of the insulating CEI, and the volume-fluctuation induced loss of electrical contact. The remaining issues for the current FeS_2@RC electrodes were identified to be the inaccessibility of some FeS_2 nanocrystals due to thick RC shells, the intrinsically limited conductivity of the RC matrix, a substantial amount of irreversible lithium consumption by the oxygen-containing functional groups, and the poor compatibility of the electrolyte solution with FeS_2. Our future research will focus on 1) synthesis of highly-dispersed colloidal FeS_2 nanocrystals to improve the uniformity of the RC encapsulation; 2) blending conductive additives (such as metallic carbon nanotubes and graphene).
into the RC precursor; 3) utilization of oxygen-free polymers such polyacrylonitrile (PAN); and 4) adoption of a better electrolyte solution of LiTFSI in TEGDME.

4.6 Acknowledgements

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4.7 References


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CHAPTER 5
MANAGING THE VOLUME FLUCTUATION OF FeS$_2$ CATHODE IN LITHIUM ION BATTERIES USING POLYACRYLONITRILE

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5.1 Abstract

Iron pyrite (FeS$_2$) is desirable as an active material for lithium ion battery cathodes due to its high energy density and has been commercialized for non-rechargeable cells since the 1980s. Unfortunately, the poor cyclability at ambient conditions has prevented its commercial use in room temperature rechargeable batteries. One promising strategy to improve the cyclability of lithium ion battery materials is the use of a conductive carbon coating. Our previous work demonstrated an improved retention ratio when FeS$_2$ nanocrystals were embedded in a resilient carbon matrix from a glucose precursor. Here we study the efficacy of polyacrylonitrile as a carbon precursor using three matrix morphologies: large diameter carbon nanotubes, flexible carbon films, and porous flexible carbon films. Micron-sized FeS$_2$ spheres were synthesized using a solvothermal method. Coatings were achieved by two methods: growth of FeS$_2$ nanorods inside the large diameter carbon nanotubes or direct mixing of FeS$_2$ powder with the precursor followed by a low-temperature carbonization of films. In the course of this study, we found a uniquely good retention ratio for our control FeS$_2$ cells compared with many literature results. Results were collected using electrochemical techniques, SEM, TEM, and XRD.

5.2 Introduction

The development of iron pyrite (FeS$_2$) as a cathode material for lithium ion batteries (LIBs) is a widely researched topic due to its high theoretical charge capacity (890 mA·h g$^{-1}$), naturally abundant elements, and environmental benignity.$^{1,2}$ The lithiation process involves the uptake of four lithium ions per FeS$_2$ unit$^{1,3-6}$ according to the following equations.$^{4,7}$

$$FeS_2 + 2Li^+ + 2e^- \rightarrow Li_2FeS_2 \quad (1)$$
$$Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow Fe^0 + 2Li_2S \quad (2)$$

In contrast to the intercalation mechanism observed in materials such as graphite and LiCoO$_2$, where lithium ions rest between layers in the crystal lattice, FeS$_2$ operates under the conversion mechanism.$^{1,8-10}$ That is, lithium reactions with FeS$_2$, resulting in separate microphases of Fe and Li$_2$S (the electro-active species). Equations 1 and 2 summarize the two phase changes that occur during discharge. At high temperatures (molten salt batteries at 400 – 450 °C) these reactions are reversible and cells have been
commercialized for large-scale military applications. However, the slower kinetics at room temperature prevent Equation 1 from being fully reversible; a maximum of 0.8 lithium ions can be extracted in that step for an overall total of 2.8 maximum lithium ions. This 1.2 lithium loss equates to a minimum 30% loss after the first discharge. Room temperature primary (non-rechargeable) batteries were commercialized in the 1980s, yet the challenge of stabilizing FeS$_2$ for use in rechargeable, room-temperature batteries is ongoing.

This seeming quandary has been attributed to a number of specific challenges: 1) poor electrical conductivity of the lithiation product, Li$_2$S; 2) slow lithium diffusion through the FeS$_2$ bulk in thin films at room temperature; 3) detrimental and irreversible reactions between the active material and the electrolyte solution causing the growth of an insulating surface layer; 4) the formation of lithium polysulfides (Li$_2$S$_n$, n>2), which are soluble in conventional electrolyte solutions and cause a loss of active material; and 5) large volume fluctuation during cycling, which causes cracking and eventual pulverization of FeS$_2$ thin films. The accumulated effect of these issues results in rapid performance failure.

A significant amount of effort has been invested into overcoming these issues through the adaptation of battery conditions or electrode architecture. Choi et al demonstrated that FeS$_2$ showed better cycling performance using lithium trifluorosulfonimide in triethyleneglycol dimethylether compared to the traditionally used lithium hexafluorophosphate in ethylene carbonate/diethylcarbonate. Mildly increased temperatures have shown dramatically improved cyclability. The primary strategies for altering electrode morphology are as follows: 1) prelithiation of the FeS$_2$ active material to minimize volume expansion; 2) decreasing FeS$_2$ particle size, which reduces the diffusion distance for ions and electrons, allows for volume expansion, and improves the contact between the electrode material and the current collector; 3) controlling the nanoarchitecture through the formation of wires or cubes; 4) utilizing synthetic FeS$_2$ due to its improved purity and morphology; and 5) coating the FeS$_2$ surface with a protective layer. The last approach offers the most benefits for FeS$_2$ due to the multivariate challenge it presents.

Surface coatings explored in battery applications have included gelatin, conductive polymers, and Li$_2$CO$_3$. One promising system to overcome the aforementioned limitations of FeS$_2$ is to provide support and protection through an elastic, conductive carbon coating. Previously we reported the hydrothermal polymerization of glucose on the surface of premade FeS$_2$ nanoparticles, followed by carbonization at 350 °C resulting in a resilient carbon composite, or FeS2@RC. It was found that the composite dramatically improved the retention ratio by protecting the FeS$_2$ and maintaining contact with the current collector, but resulted in a lower initial capacity and an irreversible capacity loss in the first
few cycles. It was concluded that the matrix contained oxygen function groups, which were irreversibly consuming lithium, due to the low temperature carbonization. Moreover, some FeS$_2$ remained electrochemically inaccessibility, lowering the initial capacity, and electrochemical impedance spectroscopy indicated poor initial conductivity of the RC matrix.

To improve on our previous results, we hypothesized we needed a different carbon precursor that was oxygen-free and could provide both ionic and electrical conductivity even when carbonized at a low temperature. Low temperature carbonization is desirable for two reasons: lower energy costs for synthesis, and to be compatible with the degradation temperature of FeS$_2$ at 500 °C. The precursor polyacrylonitrile (PAN) was chosen due to the literature reports indicating it as an excellent candidate, LIB studies with silicon and natural pyrite.

Here we report the synthesis of micron sized FeS$_2$ spheres from a solvothermal method utilizing FeCl$_3$·6H$_2$O and sulfur powder, with ethanol as the solvent in a stainless steel autoclave. FeS$_2$/lithium cells exhibited high capacity and capacity retention, forming flower-like shapes with cycling. We also demonstrate the fabrication and LIB performance of three different FeS$_2$ composites synthesized using the same method: FeS$_2$-filled large diameter carbon nanotubes (FeS$_2$@CNT, Figure 5.1A), a flexible carbon film (FeS$_2$@FC, Figure 5.1B), and a porous flexible carbon film (FeS$_2$@PFC, Figure 5.1C).

![Figure 5.1. Morphology of fabricated carbon composites: (A) FeS$_2$@CNT, (B) FeS$_2$@FC films, and (C) FeS$_2$@PFC films.](image)

### 5.3 Materials and methods

All chemicals were used as received. Ethanol (ACS grade) was purchased from Pharmco. Dimethylformamide (DMF, 99.8%, Macron), chloroform (ChromAR grade, Macron), hydrogen peroxide (30%, ACS grade, Macron), and carbon disulfide (99.95%) were purchased from Fisher. Acetylene black (35-45 nm), n-methylpyrrolidone (NMP, anhydrous, >99.5%), polyvinylidene fluoride (PVDF, >99.5%), and copper foil (99.99%, 9 µm) were purchased from MTI Corp. Iron chloride hexahydrate (FeCl$_3$·6H$_2$O, ACS grade) and aluminum foil (99.45% trace metals basis, 25 µm) were purchased from Alfa Aesar. Sulfur (99.998%), polyacrylonitrile (PAN, average MW 150,000), polystyrene-co-polyacrylonitrile (PS-co-PAN, average MW 165,000, acrylonitrile 25 wt. %), lithium foil (99.9% trace metals basis, 0.38 mm), bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%), and tetra(ethylene glycol)dimethyl ether (TEGDME,
99%) were purchased from Sigma Aldrich. Single walled carbon nanotubes (SWNTs, 90 wt. %) were purchased from Cheap Tubes. Anodic aluminum oxide (AAO, 200 nm pores) was purchased from Whatman, Inc. Nanopure water (18.3 MΩ/cm) was obtained from a Barnstead water purification system.

5.3.1 Synthesis of FeS₂ spheres

First, 0.8 mmol of FeCl₃·6H₂O (216 mg), 8 mmol of sulfur powder (256 mg), and 6 mL ethanol were added to a Teflon-lined, stainless steel autoclave (Parr Instr., model 4749, 23 mL capacity). The reactor was sealed and heated at 200 °C for 18 h in a muffle furnace. The reactor was allowed to cool to room temperature; the resulting product adhered strongly to the side of the liner and mechanical scraping was required to collect the powder. The resulting product was separated and purified via typical precipitation protocols. First, the crystals were separated from the ethanol solution using a relative centrifugal force (RCF) of 1228 G (3100 rpm on a RCF-fixed Medilite centrifuge) for five minutes. The supernatant was decanted and washed three times with chloroform to remove organic contaminants, and once in carbon disulfide to remove excess sulfur. Each washing step was also centrifuged for five minutes. Finally, the powder was dried in a vacuum desiccator overnight.

5.3.2 FeS₂@CNT synthesis

Large diameter CNTs were fabricated with a template-directed method modified from the literature. The synthesis scheme is illustrated in Figure 5.2. Anodic aluminum oxide (AAO, i) with a pore diameter of 200 nm was utilized as a template. First, a 12.5% solution of PAN in DMF was impregnated in the AAO pores via capillary force, and both sides of the AAO were wiped with a tissue to remove excess PAN. The PAN/AAO was dried at 100 °C overnight, stabilized in air at 250 °C for 20 hours in a tube furnace, and carbonized under argon at 600 °C for 1 hour (step 1). Next, the same solvothermal reaction as in Section 5.3.1 was performed with four CNT/AAO (ii) disks standing upright in a Teflon holder (step 2). After cooling, the disks were removed, rinsed with ethanol, and treated for 10

Figure 5.2. (A) Fabrication scheme for FeS₂@CNTs. (B) TEM images corresponding to each step in A.
mins in 6% aqueous hydrogen peroxide solution to remove the excess FeS$_2$ from the outside AAO surface. The FeS$_2$@CNT/AAO (iii) were finally treated with a 5% aqueous NaOH solution overnight with stirring (step 3). The FeS$_2$@CNT (iv) powder was collected via centrifugation and washed several times with water before being dried in a vacuum.

### 5.3.3 Material characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Philips X’Pert X-ray diffractometer using Cu Kα radiation. XRD samples were prepared by dropping acetone suspensions of FeS$_2$ (or FeS$_2$@RC) composites onto glass slides. Scanning electron microscopy (SEM) images were taken on a Field Emission SEM (JEOL JSM-7000F FESEM). Transmission electron microscopy (TEM) images were taken with a Philips CM200 transmission electron microscope. The TEM samples were prepared by dripping ethanol suspensions of the composite onto carbon-coated copper grids (400 mesh, Electron Microscopy Sciences) and then drying in a vacuum desiccator overnight.

### 5.3.4 Electrode fabrication

Electrodes were fabricated using a standard slurry protocol. First, the active materials of FeS$_2$ or FeS$_2$@CNT (80 wt. %) were blended well for 10 minutes by hand along with acetylene black (6 wt. %), commercial SWNTs (6 wt %), PVDF binder (8 wt. %), and a small amount of NMP in a mortar. The obtained slurry was bladed onto an aluminum foil current collector and dried at 110 °C overnight.

In the case of FeS$_2$@FC and FeS$_2$@PFC electrodes, the PVDF was replaced with PAN. The blended FeS$_2$ powder, acetylene black, and SWNT mixture was added to a pre-made, 10 wt. % solution of PAN and stirred overnight. To induce pore formation in the FeS$_2$@PFC sample, a stock solution of PS-co-PAN was made, an additional 0.8% excess PS-co-PAN was added to the slurry, and the slurry was stirred for an additional 30 minutes. The obtained slurries were blade-cast in the same fashion as the FeS$_2$ electrodes and dried overnight at 110 °C overnight. To carbonize the PAN, the electrodes were stabilized at 250 °C for 20 hours and carbonized at 300 °C for 1 hour. The lower temperature carbonization compared with the template-directed CNTs was to promote flexibility and prevent FeS$_2$ degradation. During this process, the PS-co-PAN pyrolyzes, leaving pores. For more details on the selection of PS-co-PAN, see Appendix C and Figure C.1.

All electrodes were normalized to the net mass of FeS$_2$. During carbonization, PAN loses nitrogen and hydrogen, resulting in a final mass of 68% of the starting mass. The wt. % of FeS$_2$ was therefore calculated using Equation 5.3:

$$\text{wt. % FeS}_2 = \frac{m_{\text{FeS}_2}}{m_{\text{FeS}_2} + m_{\text{AC}} + m_{\text{SWNT}} + (0.68 \times m_{\text{PAN}})}$$

5.3
5.3.5 Electrochemical measurements

Next, the electrodes were punched into small discs of 10 mm in diameter using a compact precision disc cutter (MTI Corp., MSK-T-07). The mass of FeS$_2$ per disc was usually 0.5-1 mg. After that, two-electrode split cells were assembled in an Argon-filled glove box, using the FeS$_2$ (or FeS$_2$@RC) electrode as the working electrode, lithium foil as the anode, and a 25-µm polypropylene membrane (Celgard 2500) as the separator. The assembled cells were taken out of the glove box and promptly sealed with wax to prevent any leakage. Last, the electrode performance was assessed using an 8-channel battery analyzer (MTI Corp., BST8-MA) with standard galvanostatic (constant current) charge/discharge techniques, including the gravimetric charge capacity ($Q_m$) versus cycle number, and Coulombic efficiency (CE%), where $Q_m$ is versus the net mass of FeS$_2$ and \( CE\% = \frac{Q_{m,\text{delithiation}}}{Q_{m,\text{lithiation}}} \). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a potentiostat (either a Versastat 4 by Princeton Applied Research or a Reference 600 by Gamry Instruments).

5.4 Results and discussion

The as-produced FeS$_2$ powders consisted of large (several micron) spheres mixed with irregularly shaped material (see Figure 5.3A). The FeS$_2$@CNT powders are shown in Figure 5.3B. The phase purity was confirmed using powder X-ray diffraction (XRD); the patterns for both powders matched the FeS$_2$ standard (JCPDS 01-071-0053) very well (Figure 5.3C-D and Figure C.2).

![Figure 5.3. SEM images of (A) FeS$_2$ and (B) FeS$_2$@CNT powders. XRD patterns for (C) FeS$_2$ and (D) FeS$_2$@CNT powders. The black sticks denote the patterns of pyrite FeS$_2$ standard (JCPDS 01-071-0053).](image)

5.4.1 Initial electrochemical characterizations

Cyclic voltammetry (CV) was employed as the primary electrochemical screening for all four electrodes (Figure 5.4). Cells were scanned at 0.1 mV/sec between 0.7 – 2.4 V vs. Li$^+$/Li, starting at 2.4
The first reduction peak (in blue), representing the lithiation in Equations 5.1-5.2, appears at ~1.2 V for FeS₂ and FeS₂@PFC, ~1.1 V for FeS₂@FC, and ~1.3 V for FeS₂@CNT. These shifts indicate that the highest activation energy for lithiation occurs in FeS₂@FC, likely due to a thicker coating that the other two composites. The FeS₂@CNT shows promise, shifting the peak to 1.3 V due to more favorable reaction kinetics. The subsequent lithiation peaks suggest reasonable good stability for all the cathode materials, appearing at ~1.4 V in all cases with only slight downward shifts at 20 cycles for FeS₂, FeS₂@FC, and FeS₂@PFC. Additionally, the latter two materials show an additional small peak in the initial sweep (Figure 5.4C-D), possibly indicating a lithiation of the PAN or increased ionic conductivity resulting in more obvious phase transitions for the two steps. The oxidation peaks reveal unusual behavior. The FeS₂ electrodes show a large delithiation peak, which may be due to a contaminating species being oxidized at the same potential range. The peak depletes rapidly in the first three cycles. The carbon coatings suppress this phenomenon in the first few cycles; furthermore, the oxidation peak occurring at 2 V in FeS₂ is shifted closer to the reduction peak (~1.9 V) suggesting superior reversibility. However, at 20 cycles a large, broad reduction peak emerges in all cases, signifying a breakdown of the electrode materials.

Figure 5.4. Cyclic voltammograms for (A) FeS₂, (B) FeS₂@CNT, (C) FeS₂@FC, and (D) FeS₂@PFC. Includes cycle 1 (blue), 2 (red), 3 (green), and 20 (brown).

Figure 5.5. (A) Cyclability at 0.05C and (B) retention ratio at 0.05C for all four electrodes.
The performance of these four cathodes were further investigated by cycling lithium cells over the voltage range of 1.1 – 2.4 V vs. Li⁺/Li at a rate of 0.05C (1C = 890 mA g⁻¹), as shown in Figure 5.5. The FeS₂ cathode had the best performance overall, revealing an initial discharge capacity of 850 mA·h g⁻¹ and maintaining a surprisingly stable cycling compared with the FeS₂ in Chapter 4, retaining 340 mA·h g⁻¹ after 50 cycles. This performance is comparable with high capacity nanomaterials in the literature. The carbon coated materials, in contrast, show lower initial capacities, with the FeS₂@CNT cathode exhibiting the very poor initial discharge capacity of only 200 mA·h g⁻¹. However, as displayed in Figure 5.5B, FeS₂@CNT preserves the highest retention ratio. This is likely due to the low capacity to begin with, but lines up with the more stable CV seen in Figure 5.4B. Another result of note is the improved capacity retention of FeS₂@FC. While both the FeS₂@FC and FeS₂@PFC lost 50% of the initial capacity after the first cycle compared to 40% for FeS₂, FeS₂@FC does not drop as much with cycling. Interestingly, the FeS₂@PFC cathodes presented a nearly identical retention ratio as FeS₂, but the 50% initial loss resulted in an overall much poorer performance.

5.4.2 Cycling and rate capability

To narrow the investigation to the two most promising systems, the FeS₂ and FeS₂@FC cathodes were further studied together. As demonstrated in Figure 5.6A-B the FeS₂ and FeS₂@FC cathodes exhibited initial discharge capacities of 850 and 665 mA·h g⁻¹, respectively, and both had very high CEs starting at >98%. After 40 cycles, FeS₂ retained 360 mA·h g⁻¹ and FeS₂@FC retained 265 mA·h g⁻¹. Note that the CE is calculated starting from the 2nd cycle because the first step is discharging and the 1st cycle thus does not have a charge capacity. The discharge/charge profiles (Figure 5.6C-D) displayed similar performance for both cathodes, with flat voltage plateaus at ~1.5V vs. Li⁺/Li. The overvoltages (the difference between the lithiation and delithiation plateaus) for both were also comparable at ~0.3V, consistent with literature reports.²⁷,²⁸,³³,³⁸,⁴⁹

The rate capabilities (Figure 5.6 and Figure C.3), again, demonstrate similar performance. Two major implications of note are visible, however. First, the specific capacity of FeS₂@FC at 0.05C is similar to that of FeS₂ at 0.25C, indicating the carbon coating is inhibiting the lithium diffusion kinetics. If the FeS₂@FC cells were cycled at lower rates (0.01C or lower) it is possible the initial capacity would be improved by allowing more time for lithiation. Second, at high rates (0.25C and 0.5C), the discharge plateaus become distorted, implying the electrodes are not in equilibrium through lithiation. The specific capacities at this rate are approximately equal, however, showing a slight positive effect on the equilibrium by the FC coating. This may be due to the slower kinetics. Furthermore, Figure C.3 shows the capacity retention is improved for FeS₂@FC during the 5 cycles at every rate.

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Figure 5.6. Cyclability at 0.05C, discharge/charge voltage profiles at 0.05C, and discharge/charge voltage profiles at different rates for FeS$_2$ (A-C) and FeS2@FC (D-F).

5.4.3 Conductivity and charge transfer

As seen in Figure 5.7, electrochemical impedance spectroscopy revealed unusual behavior for both electrodes. The initial cycle (0, black) of both the FeS$_2$ and FeS$_2$@FC has a very large impedance, much larger than the proceeding cycles. This may indicate an energy barrier prior to the first lithiation, dramatically increasing the charge transfer resistance (represented by the semicircle). Comparing the shape of the two, the FeS$_2$@FC has a more shallow transition between the semicircle and the line, indicating an increased diffusion limitation. This phenomenon is likely caused by slower lithium diffusion through the FC coating. In the following cycles, however, the behavior changes for the FeS$_2$@FC electrode. The semicircle deepens, implying the system is no longer diffusion limited. Both electrodes have significantly reduced charge transfer resistance ($R_{ct}$), as signified by the smaller semicircles in all cycles for 1-20. FeS$_2$@FC lags slightly in this phenomenon; cycle 0.5 (red) is larger than the rest. Between cycles 1-20, the $R_{ct}$ increases only slightly for both materials, exhibiting a fairly stable performance consistent with the capacity retention seen in Figure 5.6.

5.4.4 Electrode morphology

The final characterization was SEM imaging of uncycled electrodes, and post-mortem electrodes after 20 cycles (Figure 5.8). The cycled electrodes were washed with TEGDME solvent three times in an Argon glove box to eliminate the LiTFSI salt. They were removed and washed with hexane to get rid of the high boiling poing TEGDME and dried overnight in a vacuum desiccator. The cathodes show similar appearance before cycling (A and C), but after 20 cycles some intriguing morphology emerges (B). As indicated by the black arrows, flower-like shapes are seen sporadically throughout the topology. After
comparing the overall electrode morphology before and after cycling, it is possible that these are the result of cycling on the spheres, and may partially account for the high retention ratio of FeS$_2$. The FeS$_2$@FC, on the other hand, appears to prevent their formation.

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**Figure 5.7.** Electrochemical impedance spectroscopy of FeS$_2$ (A and C) and FeS$_2$@FC (B and D).

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**Figure 5.8.** SEM images of uncycled electrodes and post-mortem electrodes after 20 cycles for FeS$_2$ (A and B) and FeS$_2$@FC (C and D). Insets show higher magnification images. Arrows in (B) identify the flower-like morphology detailed in the inset.

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### 5.5 Conclusions

Here we have described a facile solvothermal synthesis for the formation of FeS$_2$ LIB cathodes. We applied this synthesis to a template-directed method using large diameter CNTs (200 nm) from polyacrylonitrile in an AAO template, achieving FeS$_2$@CNT composites. Furthermore, we coated the FeS$_2$ powder, comparing the effect of PAN-originated flexible (FeS$_2$@FC) and porous flexible (FeS$_2$@PFC) films. The FeS$_2$ cathodes show promise as a high capacity material due to the surprising
capacity retention. The carbon coatings unfortunately resulted in lower overall capacities, though FeS$_2$@FC provided stabilization and resulted in an improved retention ratio. Given these results, three questions arise. 1) Why does the FeS$_2$ outperform the carbon composites? 2) What feature of the synthesis or FeS$_2$ morphology leads to the high capacity retention and stability? 3) Would it be possible to exploit these features to further improve the FeS$_2$ retention ratio without the addition of a conductive coating? More experimentation is needed to develop a definitive explanation to these questions. The exploration of additional research parameters is needed to determine the effect of morphology on performance.

5.6 Acknowledgements

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5.7 References


CHAPTER 6
SUMMARY AND FUTURE WORK

6.1 General conclusions

This thesis described the research performed on the synthesis and lithium ion battery performance of iron pyrite. Solvothermal synthesis methods were performed involving two iron precursors: iron diethyldithiocarbamate and iron (III) chloride hexahydrate. In the first synthesis, three synthetic parameters were hypothesized to be crucial to the successful formation of colloidal nanoparticles; the validity of this hypothesis was explored and confirmed using a facile, air-compatible solvothermal procedure. The three parameters were high precursor solubility, the concentration of an appropriate ligand, and increased mass transport through stirring. The reaction time was also found to be important to particle stability during purification. By applying these factors to the solvothermal synthesis, colloidal dispersions of iron pyrite nanocrystals were achieved that were comparable with literature results using labor-intensive, air-free hot-injection methods. Furthermore, digestive ripening was applied, resulting in monodisperse, colloidal iron pyrite nanocrystals, which is the first time such small, monodisperse particles have been reported for this material. Both synthetic systems were explored for battery applications, to study the effect of a stabilizing carbon coating using glucose and polyacrylonitrile as carbon precursors. It was found that carbon coatings surprisingly decreased the overall capacity of the materials. However, both coatings improved the retention ratio, indicating a beneficial effect of stabilizing volume fluctuation and potentially improving contact with the current collector. Moreover, the pure iron pyrite product from the iron chloride system showed promising capacity performance and interesting morphological features after cycling.

6.2 Future work

Our current work shows promise for the colloidal materials produced and for lithium ion battery applications with some modifications. In particular, the mechanism and limitations for the digestive ripening in Chapter 3, and exploration into the synthetic parameters influencing the high capacity retention of pure iron pyrite in Chapter 5 merit further investigation.

6.2.1 Mechanistic understanding of digestive ripening

Several parameters raised interesting questions into the mechanism and limitations for this system. While in the literature digestive ripening can be applied toward very large particles, in our case the initial experiments conducted with aggregates presented limited efficacy with aggregated particles.
Additionally, more time was required to achieve observable results. Experimentation exploring these limitations using very large (micron sized) starting material may provide insight into the limitations and yield resulting from this process. Furthermore, only refluxation under air and with excess sulfur produced phase-pure iron pyrite colloids. Ripening with no sulfur or under nitrogen resulted in sulfur deficient particles (fcc FeS as characterized by XRD) or heavy aggregation (under nitrogen). XPS analysis of products under these conditions, as well as from the successful system, may provide insight into the reaction mechanism during the digestive ripening process of iron pyrite.

6.2.2 Synthetic parameters influencing battery performance

The surprising capacity retention of pure FeS₂ in Chapter 5, along with the interesting morphological features observed after cycling bears continued consideration. Further elucidation of synthetic parameters, including solvent choice (water, methanol, and butanol may influence morphology), iron to sulfur ratios during the reaction (a ten times molar excess of sulfur was employed in our studies), reaction temperatures, reaction pH, and iron sources (different iron salts may vary the morphology due to different anion effects), to achieve a more uniform morphology may provide insight into their effects on cycling stability. For instance, our materials were a mixture of irregularly shaped FeS₂ and micron-sized spheres. It is unknown if one or both of these morphologies are responsible for the good performance. Moreover, the flower-like shapes seen after cycling, which are hypothesized to be derived from cycling of the large spheres, may provide further capacity retention if synthesized as the starting material. If the synthesis parameters could be altered to achieve different shapes, investigations into the effect of particle shape on their performance would provide valuable information into the structure-performance relationship of these materials.
APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 3
IRON PYRITE NANOCRYSTAL INKS: SOLVOTHERMAL SYNTHESIS, DIGESTIVE RIPENING, AND REACTION MECHANISM

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A.1 Synthetic conditions

Four solvents were studied in the course of exploring the most effective one for synthesizing FeS2 nanocrystal (NC) inks. When using water as the solvent, we adapted a method reported in the literature and studied the ligand effect. First, 0.2 mmol of iron diethyldithiocarbamate (FeE3, 100 mg), 2 mmol of ligand, and 4 mL of water were added into a Teflon-lined stainless steel autoclave vessel (Parr Instr., model 4749, 23 mL). Then, the reactor was sealed and autoclaved at 180 °C in a preheated muffle furnace for 18 h. After cooling the reactor to room temperature in air, the solvent and the dark-grey product were separated via centrifugation at a relative centrifugal force (RCF) of 1228 G (3100 rpm on a RCF-fixed Medilite centrifuge) for five minutes. The collected solid was further washed with a mixture of chloroform and carbon disulfide for several times, until the centrifuged supernatant was clear and colorless. The obtained nanoparticles were not soluble in the solvents we tested, such as chloroform, toluene, hexane, or ethanol.

Three organic solvents tested were octadecylamine (ODA), toluene, and dimethylformamide (DMF). When using organic chemicals as the solvents, extra sulfur was necessary to produce phase-pure FeS2 NCs. For example, in the case of using toluene as the solvent, FeE3 (100 mg), sulfur (64 mg – FeE3:S ratio of 1:10, denoted as 10S), and solvent (4 mL) were added into an autoclave vessel. When the effects of ligand identity and concentration were explored, a sufficient amount of ODA was also added to result in a 0.1M – 0.5M solution. Then, the reactor was sealed and autoclaved at 180 - 240 °C for 18 h in a preheated muffle furnace. To study the effect of stirring, the reactor was put in a sand bath, and the stir plate was set at 700 rpm.
A.2 Solvent screening

A.2.1 ODA (Figure A.1)

In ODA, XRD data confirm (Figure A.1A) that nanocrystalline FeS2 was obtained in the temperature range of 190 - 240 °C. At 180 °C, some unknown impurities were also present. However, the problem remained that the obtained NCs were not soluble in any of the solvents we tested, due to the considerable amount of aggregates as shown in the TEM image (Figure A.1B). In addition, the unreacted ODA was very difficult to remove, due to its solid state at room temperature and interaction with the ligands on the FeS2 NC surfaces. Thus, ODA only was used as the passivating ligand in the following studies.

Figure A.1. Studies of the products obtained in ODA. (A) XRD data for the products synthesized at various temperatures of 180 – 240 °C, by using FeE3 + 10S and reaction duration of 18 h. (B) TEM image of the product obtained at 200 °C. Black stick pattern is for the FeS2 standard (JCPDS No. 01-071-0053).
A.2.2 Toluene (Figure A.2)

Toluene was selected as a solvent due to its capability for dissolving ODA and FeE3. Figure A.2A shows the XRD data of the obtained FeS2 NCs at temperatures between 180 and 240 °C. Unknown impurities were present in XRD profiles, as labelled with circles in Figure A.2A. To understand the origin of this phenomenon, three control experiments were conducted (Figure A.2B): FeE3 + 10S (pink), FeE3 only (cyan), and sulfur only (brown). In addition to the contaminant peaks in SI-Figure 2A, several new unknown peaks (squares) can be observed. The control study indicated that the impurities were either associated with sulfur-containing chemicals (circles, Figure A.2A-i) or side products due to deficient temperatures, matching the major peaks from Figure A.2A-ii (squares). The fact that pyrite was not produced in the absence of sulfur indicated that sulfur played a critical role in producing phase-pure FeS2 in toluene. Furthermore, while the purification process became easier compared to using ODA as the solvent, the products were still insoluble. Thus, toluene was not a suitable option.

Figure A.2. XRD studies of the products obtained in toluene. (A) XRD spectra obtained from samples produced at various temperatures between 180 and 240 °C by using FeE3 + 10 S for 18 h. (B) Shorter time durations of 2 h (red), 4 h (blue), and 6 h (green) at 200 °C. (C) Three control reactions using FeE3 + 10S (pink), FeE3 only (cyan), and S only (brown) at 200 °C for 18 h. Black stick pattern is for the FeS2 standard (JCPDS No. 01-071-0053); squares and circles denote the unknown impurities.
A.2.3 DMF (Figure A.3)

DMF was chosen as the new solvent, due to its capability of dissolving both ODA and FeE$_3$. The XRD data in Figure A.3A showed that the best temperatures were 180 °C and 190 °C. At the higher temperatures of 200 – 240 °C, surprisingly, mixtures of iron pyrite (bottom sticks and stars) and pyrrhotite Fe$_x$S$_y$ (top sticks and squares) were obtained. Learning from ODA and toluene, control reactions were also studied using only DMF without ODA. Solid product was not obtained when using only S (Figure A.3B-i). In the case of FeE$_3$ only (without extra S), some unknown impurities other than FeS$_2$ were produced (Figure A.3B-ii). After adding extra sulfur (10S), phase-pure FeS$_2$ was obtained (Figure A.3-iii).

Figure A.3. XRD spectra of the products obtained in DMF. (A) XRD data obtained from samples produced at various temperatures between 180 and 240 °C, by using FeE$_3$ + 10 S for 18 h. (B) Three control reactions using FeE$_3$ + 10 S (red), FeE$_3$ only (blue), and S only (black) at 190 °C for 18 h. Black stick pattern is for the FeS$_2$ standard (JCPDS No. 01-071-0053), the squares and top lines identify pyrrhotite, and the circles denote an unmatched impurity.
A.3 Lower ODA concentration with stirring (Figure A.4)

When a lower concentration of 0.1M ODA was combined with stirring, the increased mass transport significantly improved the dispersity of FeS$_2$ NCs. Many aggregates were present (Figure A.1A) in addition to a large amount of free particles (Figure A.1B).

![Figure A.4](image)

**Figure A.4.** TEM images of the product obtained by using 0.1M ODA in DMF with stirring at 190 °C for 22 h. (A) Panoramic view of both individual particles and aggregates, and (B) close-up of only individual particles.

A.4 The effect of ligands in DMF on synthesis of FeS$_2$ (Figure A.5)

Four additional organic ligands – ODX, DDA, OLA, and TOPO – were assessed with the stirred reaction system under the same reaction conditions as ODA. Only the TOPO system produced phase-pure FeS$_2$, as shown by the XRD data in Figure A.5A. However, the TEM images reveal that the TOPO did not effectively passivate the particles, resulting in insoluble aggregates (Figure A.5B).

![Figure A.5](image)

**Figure A.5.** (A) XRD data of the obtained products when using DMF solutions with 0.5M ODX (i), DDA (ii), OLA (iii), and TOPO (iv). All reactions were stirred, using FeE$_3$, 6S, at 190 °C for 22 h. Black stick pattern and stars are for the FeS$_2$ standard (JCPDS No. 01-071-0053). The squares and dots denote impurities that could not be matched by any of the XRD patterns in the database or any known iron sulfide standards. (B) TEM image of the product when TOPO was used (A-iv), showing only aggregates without any individual NCs.
A.5 Additional study of the surface effect on far-ir spectra (Figure A.6)

Far-IR spectra of the TOPO-passivated (red) and ligand-free (blue) FeS$_2$ NCs show positive absorption peaks for the former sample and negative peaks for the latter.

![Figure A.6](image)

*Figure A.6.* Far-IR spectra of TOPO-passivated FeS$_2$ NCs (red) and ligand-free FeS$_2$ NCs (blue).

A.6 Development of synthetic conditions for digestive ripening (Figure A.7)

As shown in Figure A.7, our initial study of digestive ripening explored the refluxation of six ligands (ODA, DDA, OA, dodecanethiol or DDT, OSA, and OSV) in toluene, using purified particles from the autoclave synthesis in Figure 3.4, main text. The ligands and solvent were chosen based on previous literature methods. The particles aggregated in toluene, so the observation of dissolved particles could be attributed to the digestive ripening process. After 3 hours no particles were observed, but after 24 hours particles could be seen in the DDA, but not in the other ligands. DDA was thus further explored as the most promising option.

![Figure A.7](image)

*Figure A.7.* Digestive ripening of purified FeS$_2$ in toluene for 24 hours. Ligands were (A) DDA, (B) OA, (C) ODA, (D) DDT, (E) OSA, and (F) OSV. The inset in (A) shows the particles formed.
A.7 The effects of atmosphere and excess sulfur on digestive ripening (Figure A.8)

For further testing with DDA, a crude solution containing polydisperse FeS$_2$ from the autoclave reaction was refluxed with 0.75M DDA in DMF, under air. Particles can be observed by TEM (Figure A.8A), but the solution was red, indicating oxidation. The reaction was conducted under nitrogen and the reaction was still red. However, XRD revealed a very poorly crystalline product matching a reference spectrum for cubic FeS (Figure A.8B-i). Therefore, to prevent sulfur loss and maintain the FeS$_2$ crystal structure, the effect of adding 6 times excess S was also studied, with reactions refluxed under air and under nitrogen. Surprisingly, the XRD showed an amorphous product under nitrogen (Figure A.8B-ii) but matched FeS$_2$ in air (Figure 3.5, main text).

![Figure A.8](image1.png)

Figure A.8. (A) TEM image of the product refluxed with DDA under air, without excess sulfur. (B) XRD spectra of the FeS$_2$ NCs digestively-ripened under nitrogen: (red) with sulfur, and (blue) without sulfur. The concentration of DDA was 0.75M, DMF was the solvent, and the ripening duration was 23 h. Black stick pattern and circles represent cubic FeS (JCPDS #04-007-3511).

A.8 Using ODA in digestive ripening (Figure A.9)

Digestive ripening was conducted with ODA under the same conditions as with DDA. The XRD data (Figure A.9A) shows that the product was still FeS$_2$. The TEM (Figure A.9B) shows that the particle dispersion and morphology were inferior to both products before the digestive ripening and the digestively-ripened product with DDA.

![Figure A.9](image2.png)

Figure A.9. (A) XRD data and (B) TEM image of the obtained product after digestive ripening for 22 h using ODA instead of DDA as the ligand, in DMF with 6S.
A.9 Additional TEMs of digestive ripening product (Figure A.10)

TEM images of different areas on the grid were taken to compare the particle size. While some areas showed particles piled on top of each other, a monolayer of NCs was observed on nearly the whole grid. Figure A.10A and B shows lower magnification images of Figure 3.5A, main text, and A.10C shows a higher magnification of the same area. Figure A.10D-F show NCs in different areas. Additionally 600 particles were measure from TEMs of different areas, producing an average size of 5.8 ± 0.8 nm.

![TEM images of different areas of the grid.](image)

A.10 Computational details (Figure A.11)

The presence of a chemical bond necessitates that there exists a ridge of charge density connecting the bound atoms as well as a saddle point, known as the bond critical point (bond CP), which sits at the local minimum along the ridge (Figure 3.6). A good deal of information about the nature of a bond can be inferred by the character of the density at the bond critical point as changes to the amount of charge ($\rho$) at a bond CP and shape of the density near the bond CP correspond to changes to the bond itself. The shape of the charge density near a given point can be well approximated by the Hessian, which has the same transformation properties of a second degree polynomial known as the representation quadric. For a bond CP the representation quadric defines a hyperboloid of two sheets, which can be parameterized by its exterior angles defined here as $2\theta$ and $2\phi$, respectively (see Figure A.11). What is important is that these angles describe the directions along which the curvature of the charge density goes to zero and therefore small values of $\theta$ and $\phi$ correspond to a flat charge density near the bond CP, while larger values of $\theta$ and $\phi$ correspond to a more pronounced ridge within the charge density. An appropriate metric that
involves both the amount of charge as well as the shape of the density was developed by Knoerr and Eberhart, who showed that the amount of charge that must be lost from a bond CP in order to “break” the bond can be approximated using:

$$\rho \sin^2(\theta) \quad \text{and} \quad \rho \sin^2(\phi) \quad (1)$$

Observed changes to calculated values for equation 1 serves as an appropriate metric for observing changes to specific bonds. Calculated values at specified bond CPs of $\rho \sin^2(\theta)$ for the non-protonated ligand, as well as protonation at a carbon and sulfur are given in Table A.1.

Table A.1. Properties of the charge density at the indicated bond critical points.

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<th>Protonation Site</th>
<th>Bond CP</th>
<th>$\rho$ [e Bohr$^{-3}$]</th>
<th>$\rho \sin^2(\theta)$</th>
<th>$\rho \sin^2(\phi)$</th>
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<tr>
<td></td>
<td></td>
<td>LDA</td>
<td>PBE</td>
<td>LDA</td>
</tr>
<tr>
<td>None</td>
<td>Fe-S</td>
<td>0.0631</td>
<td>0.055</td>
<td>0.0499</td>
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<td></td>
<td>S-C</td>
<td>0.213</td>
<td>0.207</td>
<td>0.0938</td>
</tr>
<tr>
<td>Carbon</td>
<td>S'-CH</td>
<td>0.150</td>
<td>0.138</td>
<td>0.0880</td>
</tr>
<tr>
<td></td>
<td>S''-CH</td>
<td>0.177</td>
<td>0.174</td>
<td>0.0936</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Fe-S H</td>
<td>0.0231</td>
<td>N/A</td>
<td>0.0197</td>
</tr>
<tr>
<td></td>
<td>C-S H</td>
<td>0.204</td>
<td>0.201</td>
<td>0.0978</td>
</tr>
</tbody>
</table>

When studying protonation and nucleophilic attack, geometry optimizations were used. Geometry optimization calculations, where a nucleophile (HO$^-$ or SH$^-$) is placed near the protonated carbon (within

Figure A.11. A graphical depiction of a hyperboloid of two sheets, with the geometry of the hyperboloid described by the angles $\theta$ and $\phi$. The axes $x_1$, $x_2$, and $x_3$ are the directions along the gradient of the density goes to zero, in this case $x_3$ lies along the bond path. The angles describe the direction from the bond CP along which the curvature goes to zero, thus smaller values of $\theta$ and $\phi$ indicate a more flat density near the bond CP and as such acts as a measure of the amount of density shared between atoms. See literature for further detail."^^8"
an angstrom or two), resulted in bond formation between the nucleophile and the protonated carbon. Attack from both nucleophiles resulted in the loss of a C-S bond causing the ligand to partially break away from the central Fe atom and leaving behind a free S atom attached to the Fe.

The reported results were computed using a TZ2P basis set\(^9\) and local density approximation (LDA) exchange/correlation potential.\(^{10}\) Results were also confirmed using the generalized gradient approximation exchange and correlation functional developed by Perdew, Burke, and Ernzerhof (PBE).\(^{11}\) Note: At the PBE level of calculation no Fe-S\(^1\)H bond CP could be recovered, hence why there is no data provided for that bond CP.

A.11 References


APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 4
RESILIENT CARBON ENCAPSULATION OF IRON PYRITE (FeS₂) CATHODES
IN LITHIUM ION BATTERIES

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B.1 Additional Experimental Details

B.1.1 Determination of the RC content in FeS₂@RC composite:

The RC content in FeS₂@RC composite was determined through a two-step procedure following the same principle as thermogravimetric analysis. In the first experiment, 45.8 mg of pure FeS₂ (mⁿFeS₂, initial) was heated in air for one hour at 1000 °C, leaving 23.2 mg of residue (mⁿFeS₂, residual). In the second experiment, 50.5 mg of FeS₂@RC composite (mFeS₂@RC, initial) was heated in air for one hour at 1000 °C, leaving 15.0 mg of residue (mFeS₂@RC, residual). Under these conditions, FeS₂ was converted to Fe₂O₃, as confirmed by XRD shown in Figure B.1; the RC was completely burned away, that is, mRC, residual = 0.

Thus, we can get

\[ m_{FeS_2@RC, residual} = m_{FeS_2, residual} + m_{RC, residual} = m_{FeS_2, residual} \]

Equation B.1

Based on the first experiment, we define and calculate F using Equation B.2.

\[ F = \frac{m^{n}_{FeS_2, residual}}{m^{n}_{FeS_2, initial}} = \frac{23.2mg}{45.8mg} = 0.50 \]

Equation B.2

Based on the second experiment, can get the following equations:

\[ m_{FeS_2@RC, initial} = m_{FeS_2, initial} + m_{RC, initial} \]

Equation B.3

\[ F = \frac{m_{FeS_2, residual}}{m_{FeS_2, initial}} \]

Equation B.4

\[ x = \frac{m_{RC, initial}}{m_{FeS_2@RC, initial}} \]

Equation B.5

Equation B.4 means that the conversion of FeS₂ to whatever the final residual (confirmed to be Fe₂O₃...
though) is not affected by the presence of RC, which would be completely burned away under the experimental conditions. **Equation B.5** defines $x$ as the mass fraction of RC in the composite (RC% = $x$).

Substituting B.4 and B.5 into B.3, we can get

\[
\frac{m_{\text{FeS}_2\text{RC, initial}}}{F} = \frac{m_{\text{FeS}_2, \text{residual}}}{F} + x \cdot \frac{m_{\text{FeS}_2\text{RC, initial}}}{F}
\]

\[
\Rightarrow m_{\text{FeS}_2\text{RC, initial}} = m_{\text{FeS}_2, \text{residual}} + x \cdot m_{\text{FeS}_2\text{RC, initial}}
\]

\[
\Rightarrow m_{\text{FeS}_2\text{RC, initial}} - m_{\text{FeS}_2, \text{residual}} = x \cdot m_{\text{FeS}_2\text{RC, initial}}
\]

\[
\Rightarrow x = \frac{m_{\text{FeS}_2, \text{residual}}}{m_{\text{FeS}_2\text{RC, initial}}} \cdot \frac{1}{F}
\]

Plugging the experimental data into **Equation B.6**, we can get

\[
x = 1 - \frac{15.0 \text{mg}}{0.506} \cdot \frac{1}{50.5 \text{mg}} = 0.413 = 41\%
\]

Accordingly, the fraction of FeS$_2$ in the FeS$_2$@RC composite is $1 - x = 59\%$.

---

**Figure B.1.** XRD pattern (red) of the product from burning FeS$_2$ in air at 1000 °C for one hour together with the stick pattern of standard Fe$_2$O$_3$ (black, JCPDS 00-003-0800).
Figure B.2. Morphological characterization of FeS\textsubscript{2}@RC composites obtained through hydrothermal treatment at different temperatures, reaction durations, and glucose concentrations. (a) TEM and SEM (the inset) images for 180 °C, 4h, and 0.5 M glucose; (b) TEM image for 180 °C, 2 h, 0.5 M glucose; (c) TEM image for 180 °C, 4 h, 0.1 M glucose; (d) SEM and TEM (the inset) images for 160 °C, 4 h, 0.5 M glucose; (e) SEM image for 160 °C, 8 h, 0.5 M glucose; (f) SEM image for 180 °C, 4 h, 0.5 M glucose without loading FeS\textsubscript{2}.

B.1.2 Synthesis of pure RC powder (Figure B.2f)

The pure RC powder was synthesized through the hydrothermal treatment of 0.5 M glucose at 180 °C for 4 h, followed by tube furnace carbonization at 350 °C for 4 h. The use of 160 °C for 7 h during the hydrothermal step, the same conditions as making the RC composite, could not get any collectable powder. This was ascribed to the loss of the facilitating effect of FeS\textsubscript{2} nanoparticles, which might serve as nucleation centers for RC.

Figure B.3. Cyclic voltammogram of the electrode made of resilient carbon instead of FeS\textsubscript{2} nanocrystals or FeS\textsubscript{2}@RC composite.
Calculation of the actual charge capacity of FeS$_2$ by correcting the contribution of the RC matrix:

\[
Q_{\text{corrected}} = \frac{Q_{\text{total}}^{\text{FeS}_2}}{m_{\text{FeS}_2}} = \frac{Q_{\text{total}}^{\text{FeS}_2@RC}}{m_{\text{FeS}_2}} - \frac{Q_{\text{total}}^{\text{RC}}}{m_{\text{FeS}_2}} = Q_{\text{m,FeS}_2}^{\text{apparent}} - \frac{Q_{\text{m,RC}}^{\text{m,RC}}}{m_{\text{FeS}_2}} = Q_{\text{m,FeS}_2}^{\text{apparent}} - \frac{Q_{\text{total}}^{\text{RC}}}{m_{\text{FeS}_2}} \\
= Q_{\text{m,FeS}_2}^{\text{apparent}} - Q_{\text{m,RC}}^{\text{total}} \times \frac{\text{wt}\% \text{ of RC in FeS}_2@RC}{\text{wt}\% \text{ of FeS}_2 \text{ in FeS}_2@RC}
\]

where the wt\% of RC in FeS$_2$@RC is 41\% and the wt\% of FeS$_2$ in FeS$_2$@RC is 59\%.

\[\text{B.1.3 Acknowledgements}\]

Acknowledgment is made to the Colorado School of Mines for providing YY with startup fund and the donors of the American Chemical Society Petroleum Research Fund for partial support of this research (Grant No. 52877DNI10).
APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 5

C.1 Determination of the optimal pyrolyzing carbon

Oleylamine (OA, technical grade, 70%), styrene (>99%), polystyrene-block-polybutadiene-block-polystyrene (PS-b-PBD-b-PS), benzonitrile (anhydrous, 99%), adiponitrile (99%), and dodecanenitrile (99%) were purchased from Sigma Aldrich.

PAN solutions were mixed with OA (A), styrene (B), PS (D), PS-co-PAN (E), adiponitrile (F), benzonitrile (G), and dodecanenitrile (H). **Figure C.1C** shows a 30 wt. % PS-b-PBD-PS solution with no added PAN. Films were prepared by drop-casting aluminum foil.

**Figure C.1.** SEM images of selected PFCs of the following compositions: (A) 2:1 PAN:OA as 3 wt. % solution; (B) 2:1 PAN:styrene as 3 wt. % solution; (C) 30 wt. % PS-b-PBD-PS solution; (D) 2:1 PAN:PS as 3 wt.% solution; (E) 5:1 PS-co-PAN/PAN as 10 wt. % solution; (F) 2:1 PAN:adiponitrile as 10 wt. % solution; (G) 2:1 PAN:benzonitrile as 10 wt. % solution; (H) 2:1 PAN:dodecanenitrile as 10 wt. % solution. All solutions were dissolved in DMF.
Figure C.2. (A, C, E) SEM, TEM, and XRD of as-produced large diameter CNTs, without FeS$_2$ loading. (B, D, F) SEM, TEM, and XRD of FeS$_2$@CNT powders.

Figure C.3. Rate capability of all four cathode materials.
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Date:  Nov 1, 2011  
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Publication: ACS Nano
Publisher: American Chemical Society
Date: Oct 1, 2012
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Author: James Puthussery, Sean Seefeld, Nicholas Berry, et al
Publication: Journal of the American Chemical Society
Publisher: American Chemical Society
Date: Feb 1, 2011
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Author: Sean Seefeld, Moritz Limpinsel, Yu Liu, et al
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