A Stabilized PAN-FeS₂ Cathode with an EC/DEC Liquid Electrolyte

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In this study we embed phase pure natural cubic-FeS₂ (pyrite) in a stabilized polycrylonitrile (PAN) matrix. The PAN matrix confines FeS₂’s electroactive species (Fe⁰ and S₈⁻) for good reversibility and efficiency. Additionally, the stabilized PAN matrix can accommodate the 160% volume expansion of FeS₂ upon full discharge because it is not fully carbonized. At room temperature, our PAN-FeS₂ electrode delivers a specific capacity of 470 mAh g⁻¹ on its 50th discharge. Using high-resolution transmission electron microscopy (HRTEM) we confirm that FeS₂ particles are embedded in the PAN matrix and that FeS₂’s mobile electroactive species are confined during cycling. We also observe the formation of orthorhombic-FeS₂ at full charge, which validates the results of our previous all-solid-state FeS₂ battery study.

The energy density of conventional Li-ion batteries with LiMO₂ (M = transition metal) cathodes and graphitic anodes is approaching a practical upper limit after two decades of optimization. In order to improve the energy density of Li-ion batteries further, new cathodes must be developed with capacities exceeding the formation of orthorhombic-FeS₂ at full charge, which validates the results of our previous all-solid-state FeS₂ battery study.

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The energy density of conventional Li-ion batteries with LiMO₂ (M = transition metal) cathodes and graphitic anodes is approaching a practical upper limit after two decades of optimization. In order to improve the energy density of Li-ion batteries further, new cathodes must be developed with capacities that compare to those of advanced anodes such as Si.[1] The FeS₂ conversion chemistry is a promising candidate to replace the LiMO₂ intercalation chemistry because FeS₂ is inexpensive, energy dense, and environmentally benign. The four electron reduction of cubic-FeS₂ (pyrite) with lithium (FeS₂ + 4Li⁺ + 4e⁻ → Fe⁰ + 2Li₂S) provides a specific capacity of 894 mAh g⁻¹, whereas, the very best LiMO₂ intercalation cathodes can only provide 200 mAh g⁻¹.[2–4] For these reasons, Energizer popularized the FeS₂/Li chemistry as a primary battery,[8] but a secondary FeS₂/Li battery is not yet commercially available. The safety issues associated with lithium metal anodes can be cited as one obstacle obstructing the realization of a rechargeable Fe₁₋ₓSₓ/Li battery.[6] however, the FeS₂ cathode also presents very difficult problems. This paper addresses the problems of the cathode by embedding natural pyrite in a commercially available, stabilized PAN matrix.

The problems associated with a rechargeable FeS₂ cathode can be understood by considering the electroactive species of FeS₂ during cycling. Though still the subject of much debate, a proposed reaction mechanism for cubic-FeS₂ at low temperatures is provided below for an initial discharge and subsequent charge.[3,7,8] From Equation (2) we see that small aggregates of superparamagnetic Fe⁰ atoms are one product of the reduction of FeS₂ with four Li⁺. Fe⁰ particles have an average diameter of 3.6 nm and are highly reactive in order to catalyze the oxidation of the other full discharge product, Li₂S, which is highly resistive. Unfortunately, nano-Fe⁰ particles tend to agglomerate into non-reactive α-Fe particles which result in the electrochemical isolation of Li₂S and a rapid loss of battery capacity.[7,9]

From Equation (5) it is also evident that cubic-FeS₂ is not reformed at full charge. Our previous work found that the charge products of an all-solid-state cubic-FeS₂ cathode are a multiphase mixture of ortho-FeS₂ (marcasite), FeS₈, and S.[7] Prior to this study it was generally accepted that the charge products were only Fe₃S₄ and S from the disproportionation of an Li₂FeS₂ intermediary phase.[11] This work will provide further evidence that ortho-FeS₂ is a charge product at ambient temperature. More importantly, the reversibility and efficiency of FeS₂ batteries will suffer from the same problems as that of a Li-S battery because sulfur is one of the three proposed charge products. The initial reduction of sulfur produces soluble and highly mobile polysulfides (Sₙ⁻). The dissolution of these polysulfides into an organic liquid electrolyte contributes to capacity fade and results in a parasitic redox shuttle that reduces charging efficiency.[10–12]

Initial Discharge

\[
\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{FeS}_2 \quad (1)
\]

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

Subsequent Charge

\[
\text{Fe}^0 + 2\text{Li}_2\text{S} \rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \quad (3)
\]

\[
\text{Li}_2\text{FeS}_2 \rightarrow \text{Li}_2\text{−xFeS}_2 + \text{xLi}^+ + \text{xe}^- (0.5 < x < 0.8) \quad (4)
\]
Li_{2−x}FeS_2 → 0.8 \text{ ortho-FeS}_2 + 0.2\text{FeS}_{8}\gamma + 0.175S + (2−x)Li^+ + (2−x)e^− \quad (5)

The mobility of Fe\(^0\) and polysulfides in organic liquid electrolytes explains why conventional FeS\(_2\) cathodes are not reversible. An all-solid-state battery architecture is uniquely capable of confining the electroactive species of FeS\(_2\)\(^{[9,15]}\) and we recently demonstrated the full reversibility of FeS\(_2\) as a cathode versus lithium metal at 60 °C.\(^{[7]}\) Although this study represents a milestone for the secondary FeS\(_2\) conversion chemistry, it is still more desirable to incorporate FeS\(_2\) into a conventional liquid or polymer battery because the manufacturing processes associated with conventional batteries are mature. Prior to our work, many studies attempted to use composite polymer electrolytes to confine FeS\(_2\)’s electroactive species.\(^{[4,14]}\) Unfortunately, none of these studies could demonstrate acceptable reversibility because polymer electrolytes do not provide sufficient confinement. More recently, other studies have examined the cycle ability of synthetic FeS\(_2\)/carbon and FeS\(_2\)/PANI composites in liquid electrolytes with limited success.\(^{[4,11,15,16]}\)

Here, we embed FeS\(_2\) in a stabilized PAN matrix that confines electroactive species to prevent active material loss and improve Coulombic efficiency (CE). Stabilized PAN enables the reversibility of FeS\(_2\) by considering the need to not only confine FeS\(_2\)’s electroactive species but also to accommodate FeS\(_2\)’s expansion. The effectiveness of stabilized polymers as confining matrices has been previously demonstrated with PAN-S and PANI-S composites.\(^{[17,18]}\) It has also been shown that thin coatings of stabilized PAN can accommodate the 300% volume expansion of nano-Si particles.\(^{[19]}\) By avoiding the full carbonization of PAN the elastic properties of the PAN precursor can be retained, while the conjugation of PAN during the stabilization process provides good electronic conductivity.\(^{[20]}\) More importantly, the preparation of the PAN-FeS\(_2\) composite is simple and the precursors are inexpensive, commercially available natural pyrite and PAN. The results of this study will demonstrate that the challenges associated with a conventional FeS\(_2\) cathode can be overcome.

**Figure 1.** a) Cross-sectional SEM image of an uncycled PAN-FeS\(_2\) electrode. b) TEM image with EELS zero-loss mode of the stabilized PAN matrix (light) and embedded FeS\(_2\) particles (dark). c) EELS elemental mapping of C (red), Fe (blue), and S (green).

Two electrodes were characterized electrochemically using a constant current, constant voltage (CCCV) cycling protocol. The first electrode was made with the PAN-FeS\(_2\) electrode material presented in Figure 1 while the second electrode is a control sample, which we call bare FeS\(_2\). Both cells were cycled between 1 V and 3 V at a rate of 0.1 C for all cycles. The cyclic stabilities and CE of the PAN-FeS\(_2\) (red) and bare FeS\(_2\) (orange) electrodes are provided in Figure 2a. Bare FeS\(_2\) delivers an initial discharge capacity of 828 mAh g\(^−1\), which is close to FeS\(_2\)’s theoretical capacity of 894 mAh g\(^−1\). Bare FeS\(_2\) has a notably low initial CE of 63% along with a consistently low cycling CE, drastically hindering its capacity retention so that by the 20th cycle it delivers a discharge capacity of only 120 mAh g\(^−1\), or only 14% of its initial discharge capacity. Though PAN-FeS\(_2\) delivers a lower initial discharge capacity of 729 mAh g\(^−1\), its cyclic stability and CE are greatly improved compared to bare FeS\(_2\). With a significantly improved initial CE of 94%, our PAN-FeS\(_2\) electrode delivers 470 mAh g\(^−1\), a discharge capacity retention value of 64%, with a CE approaching 99.25% by the 50th cycle. Other FeS\(_2\)-C composite electrodes showed at most ~350 mAh g\(^−1\) by the 40th cycle.\(^{[4,15]}\) PAN-FeS\(_2\) not only exceeds capacities shown by previous work, but it is also unique in that the precursors are commercially available natural pyrite and PAN.\(^{[4,14]}\) Figure 2b,c provide the voltage profiles for PAN-FeS\(_2\) and bare FeS\(_2\), respectively. The stable capacity of PAN-FeS\(_2\) is correlated with voltage profiles that are more stable compared to that of bare FeS\(_2\). With cycling, bare FeS\(_2\)’s voltage profiles develop overpotentials and lose the upper charging voltage plateau at approximately 2.4 V.

To better understand the mechanism behind the improved stability of the PAN-FeS\(_2\) electrode and identify the phases present at full charge, we use TEM and EELS to study the...
Figure 2. a) Cyclic stability of the stabilized PAN-FeS$_2$ electrode versus that of a bare FeS$_2$ electrode. Specific capacity is reported with respect to the mass of the FeS$_2$ active material. b) Voltage profiles of PAN-FeS$_2$. c) Voltage profiles of bare FeS$_2$.

Figure 3. a) TEM image of an embedded FeS$_2$ particle in a PAN-FeS$_2$ electrode collected after completion of its 10th charge. b) High resolution (HR) image of the FeS$_2$ particle in panel (a) and the corresponding FFT pattern matched with orthorhombic-FeS$_2$ along the [01–1] zone axis. c) EELS elemental mapping for Fe. d) EELS elemental mapping of S.

is consistent with our previous all-solid-state FeS$_2$/Li battery study where we observed ortho-FeS$_2$ as a charge product. It is the first time that ortho-FeS$_2$ has been observed in an ambient temperature battery because the aforementioned all-solid-state FeS$_2$ sample was recovered after charging at 60 °C. Later in the discussion we will analyze the differential capacities ($dQ/dV$) of the two electrodes presented in Figure 2 in order to provide further evidence that Equation (5) is the valid reaction for FeS$_2$'s final charging step.

Figure 3c,d display the EELS elemental mapping of Fe and S while Supporting Information Figure S5 shows the zero-loss and the EELS mapping of C for the same particle. After cycling, it is clear that there is no migration of S or Fe into the stabilized PAN matrix. This result suggests that the stabilized PAN matrix completely obstructs the dissolution of intermediate polysulfides into the liquid electrolyte and prevents the reaction of Fe$^0$ with the liquid electrolyte. Confinement of polysulfides explains why PAN-FeS$_2$ exhibited a higher CE than bare FeS$_2$. By confining polysulfides in PAN the parasitic shuttle mechanism, which reduces charging efficiency, cannot be initiated. It also suggests that our stabilized PAN is not very porous to accommodate the passage of solvated polysulfides. Supporting this idea, we measured the Brunauer- Emmett-Teller (BET) porosity of PAN-FeS$_2$ to be only 1.50 m$^2$ g$^{-1}$. Because PAN-FeS$_2$ has such a low porosity, it also suggests that it is difficult for the liquid electrolyte to impregnate the stabilized PAN matrix. Previously, we have found that stabilized PAN is electrochemically active and stable against the liquid electrolyte between 50 mV and 1 V.$^{15}$ Here, we also show PAN's electrochemical stability within a voltage window of 1 V to 3 V after running parallel experiments to those.
reported in this work with cells only containing stabilized PAN and no FeS₂ (Supporting Information Figure S6). We suspect that stabilized PAN is a mixed conductor, however, more work is currently underway to characterize its conductive properties.

We have shown that elemental S and Fe are not observed in our stabilized PAN matrix after cycling which verifies the complete confinement of FeS₂’s intermediary electroactive species. However, we still observe some capacity fade. To explain this, some FeS₂ particles are not fully embedded within our stabilized PAN matrix during material preparation so they are subject to attack by the liquid electrolyte during cycling. To fully coat every particle, we propose a direct electrode blading with stabilized PAN as previously described. In this way, partially embedded FeS₂ particles will be protected by a secondary protective coating of stabilized PAN.

As stated earlier, FeS₂ and S were generally believed to be the final charge products of a low temperature FeS₂ battery. Reductive dQ/dV analysis in the range of 2.0 V to 2.8 V (Figure 4) can be used to differentiate the direct reduction of S from the reduction of ortho-FeS₂ and lend further support to the validity of Equation (5). Supporting Figure S7 provides the dQ/dV for both PAN-FeS₂ and bare FeS₂ in the whole voltage range of 1 V to 3 V. As expected we observe three peaks in the range 2.0 to 2.5 V: one for ortho-FeS₂ (2.1 V) and two for sulfur (2.2 V and 2.5 V). The peak at 2.5 V is not a side reaction because if it were it would have also been observed during the initial discharge, however, because sulfur was not yet present the peak is also not present. The peak at 2.1 V corresponds to the reduction of ortho-FeS₂ to Li₂FeS₂ (Equation (1)), whereas the peaks at 2.5 and 2.2 V correspond to the reduction of S (Equations (6), (7), and (8)). During the initial discharge the reduction of cubic-FeS₂ occurs at 1.5–1.7 V, while on subsequent cycles the reduction of ortho-FeS₂ occurs at 2.1 V. The explanation for the difference may be related to a change in microstructure or kinetics.

In a liquid cell the direct reduction of sulfur occurs in two steps even though the thermodynamic phase diagram suggests only one plateau. The reduction of S follows a three step process as presented below. The first step, Equation (6), occurs at a higher voltage than the other two steps because the mobility and molecular nature of the polysulfides improves the reaction kinetics. Sulfur does not exhibit two plateaus in an all-solid-state structure because polysulfides are confined such that their reduction does not enjoy a kinetic advantage. The presence of two sulfur plateaus for PAN-FeS₂ suggests that some polysulfides are mobile in the liquid electrolyte and that the confinement of FeS₂ is incomplete. This corroborates our previous observation that some FeS₂ particles are not fully embedded in the PAN matrix.

\[
\begin{align*}
S + 4Li^+ + 4e^- & \rightarrow 2Li_2S_4 \quad (6) \\
Li_2S_4 + 2Li^+ + 2e^- & \rightarrow Li_2S_2 \downarrow \quad (7) \\
Li_2S_2 + 2Li^+ + 2e^- & \rightarrow 2Li_2S \quad (8)
\end{align*}
\]

In summary, the performance of the PAN-FeS₂ composite cathode suggests that the problems associated with the mobility of FeS₂’s electroactive species can be addressed without the need for a costly all-solid-state battery structure. By the 50th cycle our PAN-FeS₂ electrode delivers 470 mAh g⁻¹, or 64% of its initial discharge capacity with a CE approaching 99.25%. When viewed alongside a recent development regarding dendrite-free lithium metal anodes, the results of our stabilized PAN-FeS₂ cathode study suggest that a practical, safe conventional secondary FeS₂/Li battery is close to reality. Moreover, we also observed ortho-FeS₂ (marcasite) as a full charge product which is a first for conventional liquid batteries and validates the results of our previous all-solid-state FeS₂ battery study.

**Experimental Section**

First, naturally occurring pyrite (FeS₂, Alfa Aesar) was mechanically ground at 400 rotations per minute (RPM) for 1 h using a planetary ball mill (Across International) in order to reduce the average particle size. Next, ball milled FeS₂ and PAN (MW = 150 000 g mol⁻¹, Sigma Aldrich) were mixed in a mass ratio of 7:3, respectively, using a mortar and pestle. The mixture was then dissolved in N,N-dimethylformamide...
A cathode slurry was prepared by combining PAN-FeS$_2$, acetylene black (Alfa Aesar), and PVDF (poly(vinylidene fluoride), Alfa Aesar) binder in a 60:20:20 weight ratio, respectively, with a 1-methyl-2-pyrrolidinone (NMP, Alfa Aesar) solvent. The slurry was coated on Al foil, dried under air, and then calendared. On average, the FeS$_2$ active material loading is 1.5 mg cm$^{-2}$, and the area of each of the tested electrodes was of 1.33 cm$^2$. Test coin cells (2032, Pred Materials) were assembled with the prepared PAN-FeS$_2$ working electrode, a lithium metal foil counter electrode (Alfa Aesar), a glass fiber separator (Whatman, GF/G), and 1.5 M LiPF$_6$ in ethylene carbonate, diethyl carbonate (50:50, Soulbrain) electrolyte. The test cells were cycled using a constant current, constant voltage (CCCV) testing protocol between the voltage range of 1 V and 3 V at a constant rate of 0.1C. The voltage is held constant at 3 V at the end of each charging cycle for 30 min.

The microstructure of PAN-FeS$_2$ structure was investigated by analytical TEM (TECNAI F20 equipped with EELS) operating at 200 keV. As previously described, the TEM samples were prepared by sectioning a cycled electrode using a FIB’s Ga$^+$ beam (FEI, NOVAC200 dual beam system).[23]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by the National Science Foundation (NSF, CHE-1231048). Work at Seoul National University was supported by a grant from the Center for Iron and Steel Research Institute of Advanced Materials (RIAM, D-BB04–11, CHE-1231048). Work at Seoul National University was supported by a grant from the Center for Iron and Steel Research Institute of Advanced Materials (RIAM, D-BB04–11, CHE-1231048). Work at Seoul National University was supported by a grant from the Center for Iron and Steel Research Institute of Advanced Materials (RIAM, D-BB04–11, CHE-1231048).

Received: August 2, 2013
Revised: August 26, 2013
Published online: October 11, 2013