

Local Structure Evolution and Modes of Charge Storage in Secondary Li–FeS₂ Cells

Megan M. Butala,^{*,†} Martin Mayo,^{‡,§} Vicky V. T. Doan-Nguyen,^{§,||} Margaret A. Lumley,^{†,||} Claudia Göbel,[†] Kamila M. Wiaderek,[⊥] Olaf J. Borkiewicz,[⊥] Karen W. Chapman,[⊥] Peter J. Chupas,[⊥] Mahalingam Balasubramanian,[⊥] Geneva Laurita,^{†,§} Sylvia Britto,[#] Andrew J. Morris,^{*,‡} Clare P. Grey,^{*,#} and Ram Seshadri^{*,†,||}

[†]Mitsubishi Chemical Center for Advanced Materials, Materials Department, and Materials Research Laboratory, University of California, Santa Barbara, California 93106, United States

[‡]Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom

[§]California NanoSystems Institute, University of California, Santa Barbara, California 93106, United States

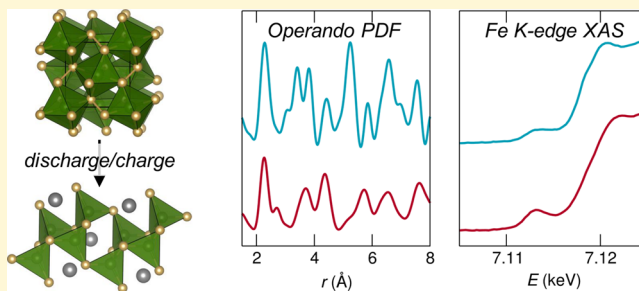
^{||}Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

[⊥]X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States

[#]Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

S Supporting Information

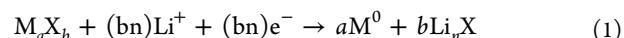
ABSTRACT: In the pursuit of high-capacity electrochemical energy storage, a promising domain of research involves conversion reaction schemes, wherein electrode materials are fully transformed during charge and discharge. There are, however, numerous difficulties in realizing theoretical capacity and high rate capability in many conversion schemes. Here we employ *operando* studies to understand the conversion material FeS₂, focusing on the local structure evolution of this relatively reversible material. X-ray absorption spectroscopy, pair distribution function analysis, and first-principles calculations of intermediate structures shed light on the mechanism of charge storage in the Li–FeS₂ system, with some general principles emerging for charge storage in chalcogenide materials. Focusing on second and later charge/discharge cycles, we find small, disordered domains that locally resemble Fe and Li₂S at the end of the first discharge. Upon charge, this is converted to a Li–Fe–S composition whose local structure reveals tetrahedrally coordinated Fe. With continued charge, this ternary composition displays insertion–extraction behavior at higher potentials and lower Li content. The finding of hybrid modes of charge storage, rather than simple conversion, points to the important role of intermediates that appear to store charge by mechanisms that more closely resemble intercalation.



INTRODUCTION

Detailed mechanistic understanding of the processes associated with the intercalation cathode material LiCoO₂ and related layered transition metal oxides has been essential to the development of modern Li-ion batteries.¹ In contrast, conversion reaction-based schemes for Li-ion batteries have not advanced as rapidly.^{2,3} Conversion reaction batteries involve electrodes that are not topochemical in their mode of charge storage and instead undergo dramatic structural and compositional changes during cycling. The broad range of chemistries (including oxides, fluorides, and sulfides) and structures capable of storing charge by conversion make it difficult to elucidate mechanistic trends that are applicable across the many candidate materials.

A general trend of conversion systems is the first discharge reaction, which can be considered for a transition metal (*M*) anion (*X*) compound as (eq 1):



Another established phenomenon in conversion systems is the significant nanostructuring that accompanies the phase changes during the first discharge.^{4,5} The formation of new interfaces during the first discharge is accompanied by a large overpotential and results in cycling products with limited long-range order, if any. The disordered nature of products contributes to the difficulty of elucidating the mechanism of charge storage and makes average structure methods, including X-ray diffraction (XRD), ill-suited to the study of conversion systems.^{6,7} Rather, local structure methods, including pair distribution function (PDF) analysis and X-ray absorption

Received: January 6, 2017

Revised: March 9, 2017

Published: March 27, 2017

spectroscopy (XAS), are powerful in studying such systems.^{8–10} A number of studies applying PDF to Fe-based conversion electrode materials have greatly contributed to the mechanistic understanding of conversion systems.^{4,5,11–13} In particular, *operando* characterization provides valuable information about the charge storage mechanism as the chemistry is occurring.

FeS₂ has compelling performance relative to other conversion materials, including transition metal oxides, and was originally investigated as a cathode for high-temperature batteries with molten salt electrolytes.^{14,15} It was later studied for room temperature secondary batteries with organic electrolytes,^{16,17} with a focus on the mechanism of charge storage. A primary Li–FeS₂ battery has since been commercialized by Energizer.¹⁸ Recent work by Shao-Horn and co-workers revisited earlier mechanistic studies.¹⁹ Near-theoretical storage by FeS₂ in an all-solid state cell operating at 60 °C has been reported recently,²⁰ as have cells based on ionic liquid electrolytes.²¹

In pyrite FeS₂, Fe²⁺ forms a face-centered cubic lattice with each Fe octahedrally coordinated by disulfide bonds of the form

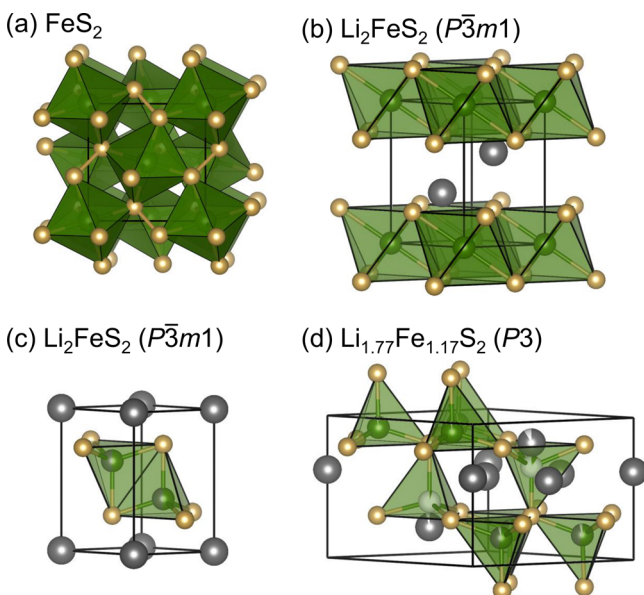
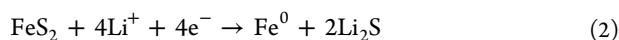


Figure 1. (a) FeS₂ (*Pa* $\bar{3}$) consists of a *fcc* lattice of Fe atoms (green) octahedrally coordinated by disulfides, highlighted in yellow. Published Li–Fe–S ternary phases proposed to be intermediate products during the cycling of FeS₂: (b) Li₂FeS₂ (*P* $\bar{3}$ *m*1) with layers of FeS₆ octahedra with Li (gray) in tetrahedral sites between the layers,¹⁷ (c) Li₂FeS₂ (*P* $\bar{3}$ *m*1) with layers of mixed occupancy Li and Fe tetrahedrally coordinated by S,²² and (d) Li_{1.77}Fe_{1.17}S₂ (*P*3) with mixed and partial occupancy (white) of Li and Fe in corner-sharing tetrahedra.²³

S₂²⁻ (Figure 1a). FeS₂ can theoretically store 4 mol of Li per formula unit, with a complete first discharge (eq 2):



FeS₂ is not recovered when charged at room temperature,²⁴ and consequently eq 2 is representative of only the very first discharge. With some exceptions,⁹ including for FeS₂,²⁵ mechanistic studies of conversion materials have typically focused on the first discharge or first cycle.^{19,26,27} The first discharge is unique from subsequent cycles, and consequently, monitoring structural evolution after the first discharge is

essential to elucidating processes representative of battery performance.

For FeS₂, there is near consensus that an intermediate phase forms during cycling. Pyrrhotite and other off-stoichiometry binaries are among those proposed,^{27–29} while other literature suggests a ternary Li–Fe–S intermediate stable over a range of Li compositions.^{24,25,30} Among the postulated ternary intermediates are those with layers of FeS₆ octahedra with Li in the van der Waals gap (Figure 1b),^{17,31} layers of Li and Fe tetrahedrally coordinated by S between layers of LiS₆ octahedra (Figure 1c),²² or a three-dimensionally connected, disordered structure with mixed and partial occupancies of Li and Fe tetrahedrally coordinated by S (Figure 1d).²³

We report new mechanistic and structural information about the reaction of FeS₂ with Li based on *operando* and *ex-situ* local structure methods. The nature of the local structure of products at various states of charge is consistent from complementary *operando* PDF and *ex-situ* XAS data. Ternary structures predicted by first-principles calculations are in good agreement with the PDF data of intermediate and charge products. The mechanism(s) of charge storage for FeS₂ depend(s) on cycling conditions including rate, temperature, and electrolyte. We focus on later cycles, as stated earlier, and find for the applied conditions dual mechanisms including (i) conversion between small, disordered domains that locally resemble Fe and Li₂S and a Li–Fe–S ternary local structure with tetrahedrally coordinated Fe at low potentials and high Li content and (ii) insertion-extraction behavior of the ternary structure at high potentials and low Li content.

EXPERIMENTAL AND THEORETICAL METHODS

Ex-Situ Cell Assembly, Cycling, and Sample Preparation.

Cycling was carried out in Swagelok cells with loose-powder electrodes of FeS₂ (Alpha Aesar, 99.9%) and conductive carbon additive Ketjen Black (KB) (AkzoNobel EC-600JD) in a 9:1 ratio by weight. Powders were ground in air with an agate mortar and pestle. LiPF₆ (1 M) in ethylene carbonate–dimethyl carbonate (EC–DMC) (1:1 ratio by volume) electrolyte and two Whatman glass filter dryer (GFD) separators were used. Li metal served as both the counter and reference electrode in these half-cells. Cells were assembled in an Ar-filled glovebox and cycled galvanostatically at a rate of *C*/40 (*Q*/10), calculated for the theoretical reaction of FeS₂ with 4 mol of Li (per formula unit) in 40 h, with potential limitations of 1 and 3 V for discharge and charge, respectively. Cells were cycled using a Bio-Logic VMP-3.

For *ex-situ* total scattering and X-ray absorption spectroscopy (XAS), loose-powder Swagelok cells were cycled to a specified potential or capacity. Cells were disassembled in an Ar glovebox, and the cathode powder was collected, washed with DMC, and dried under vacuum. For total scattering experiments, washed powders were loaded into 1.2 mm diameter kapton tubes sealed with epoxy at both ends. For XAS, powders were painted into homogeneous films on kapton tape. All *ex-situ* samples were prepared and transported under Ar.

First-Principles Calculations. Structure prediction was performed using the *ab initio* random structure searching (AIRSS) method.³² For a given system, AIRSS initially generates random structures, which are then relaxed to a local minima in the potential energy surface (PES) using density functional theory (DFT) forces. By generating large numbers of relaxed structures it is possible to widely cover the PES of the system. On the basis of general physical principles and system-specific constraints, the search can be biased in a variety of sensible ways.³³ About 2200 Li–Fe–S structures were generated by AIRSS at stoichiometries of *x* = 0.5, 1, 1.5, 2, 3, and 4 in Li_{*x*}FeS₂.

AIRSS calculations were undertaken using the CASTEP DFT plane-wave code.³⁴ The gradient corrected Perdew Burke Ernzerhof (PBE)

exchange-correlation functional³⁵ with spin-polarization was used in all calculations presented in this work. The core electrons were described using Vanderbilt “ultrasoft” pseudopotentials, and the Brillouin zone was sampled using a Monkhorst–Pack grid³⁶ with a k -point spacing finer than $2\pi \times 0.07 \text{ \AA}^{-1}$. The plane wave basis set was truncated with a cutoff value of 350 eV.

The thermodynamical phase stability of a system was assessed by comparing the free energy of different phases. From the available DFT total energy of a given binary phase of elements A and B , $E\{A_a B_b\}$, it is possible to define a formation energy per atom as eq 3:

$$E_f/\text{atom} = \frac{E\{A_a B_b\} - aE\{A\} - bE\{B\}}{a + b} \quad (3)$$

The formation energies of each structure were then plotted as a function of the B element concentration, $u = b/(a + b)$, starting at $u = 0$ and ending at $u = 1$. A convex hull was constructed between the chemical potentials at $(u, E_f/\text{atom}) = (0,0);(1,0)$ by drawing a tie line to join the lowest energy structures, which is valid provided it forms a convex function. This construction gives access to the 0 K stable structure, as the second law of thermodynamics demands that the (free) energy per atom is a convex function of the relative concentrations of the atoms.

Average voltages for the structures lying on the hull were calculated from the available DFT total energies. For two given phases on the hull, $A_{x_1}B$ and $A_{x_2}B$ with $x_2 > x_1$, the following two-phase reaction is assumed as eq 4:



The voltage, V , is given by eq 5,³⁷

$$V = -\frac{\Delta G}{x_2 - x_1} \approx -\frac{\Delta E}{x_2 - x_1} = -\frac{E(A_{x_2}B) - E(A_{x_1}B)}{x_2 - x_1} + E(A) \quad (5)$$

where it is assumed that the Gibbs energy can be approximated by the internal energy, as the pV and thermal energy contributions are small.³⁷

The low energy structures obtained by the AIRSS search were refined with higher accuracy using a k -points spacing finer than $2\pi \times 0.03 \text{ \AA}^{-1}$ and an energy cutoff of 800 eV with more accurate pseudopotentials (see the Supporting Information). The DFT+ U approach implemented in CASTEP was used to correct self-interaction error in the GGA by adding the U parameter to the d orbital of the transition metal.³⁸ The U parameter can be chosen to assimilate any experimental band gap. U parameters ranging from 2 eV to over 5 eV have been reported for first-principles calculations of various transition metal chalcogenides.^{39–41} We have used a value of $U_{\text{eff}} = 4 \text{ eV}$, as was used for Li–Fe–S–O compounds,⁴² which falls within the range of reported U values.

X-ray Absorption Studies. *Ex-situ* XAS at the Fe K -edge was carried out at 20-BM-B at the Advanced Photon Source at Argonne National Laboratory for cells cycled at C/40, as described above. Spectra were collected in transmission mode. The data was calibrated to 7.112 keV⁴³ and normalized by aligning the E_0 for each Fe foil to a reference spectra. Data was deglitched, normalized and averaged using the open source program ATHENA.⁴⁴

Operando Pair Distribution Function Studies. *Operando* total scattering experiments were carried out at 11-ID-B at the Advanced Photon Source at Argonne National Laboratory. A PerkinElmer amorphous Si-based area detector enabled rapid-acquisition of X-ray scattering measurements with an X-ray wavelength of 0.2112 Å ($\approx 58 \text{ keV}$). An AMPIX electrochemical cell⁴⁵ was assembled in an Ar-filled glovebox with a free-standing pellet cathode composed of FeS₂–graphite/VulcanC (1:1 by weight)–polytetrafluoroethylene (70:20:10 by weight). The free-standing pellet cathode was about 160 μm thick and 13 mm in diameter. The electrolyte was 1 M LiPF₆ in EC–DMC in a 3:7 by volume, which soaked a GFD separator. Li metal served as both a reference and counter electrode. The cell was galvanostatically cycled with an applied current of 0.8722 mA and a C-rate of about

C/17, based on the reaction of 1 mol of FeS₂ with 4 mol of Li in 17 h and with potential limits of 1 and 3 V. Because of time constraints of beamtime and our interest in characterizing later cycles in addition to the first discharge, *operando* studies were carried out at a faster rate than other cycling discussed here.

The background contribution of the *operando* cell was collected using an AMPIX cell assembled without the cathode. Experimental geometries were calibrated using CeO₂ powder and Fit2D freeware.⁴⁶ Fit2D was also used to integrate collected 2D data, which was acquired once every 30 min. From each set of integrated data, the real-space pair distribution function (PDF) was calculated by a Fourier transform using PDFgetX2,⁴⁷ with the structure factor taking into account the relative Li content based on a constant Fe–S ratio of 1:2 and with a $Q_{\text{max}} = 19 \text{ \AA}^{-1}$. PDFgui⁴⁸ was used to simulate PDFs and to fit data to published and calculated structures. Similar data collection and processing were carried out for *ex-situ* PDFs. Principal component analysis (PCA) was used to assess the local structure evolution during the first discharge. PCA was carried out using Origin Pro (OriginLab, Northampton, MA), which yielded three significant principle components (PCs). Linear combinations were taken of the raw PCs such that there was a single component at the beginning of the reaction and a single component at the end of the reaction.⁴⁹ The weightings for these revised PCs were evaluated with a least-squares linear combination analysis.

RESULTS

Electrochemical Cycling of FeS₂. For the first several cycles of FeS₂ unoptimized loose-powder Swagelok cells in carbonate electrolytes, we saw surprising reversibility and Coulombic efficiency (Figure 2). The discharge–charge curves give clues about the mechanism(s) of Li storage. For example, there is ambiguity as to the presence of one or two plateaus in the first discharge (Figure 2a), which would suggest either one

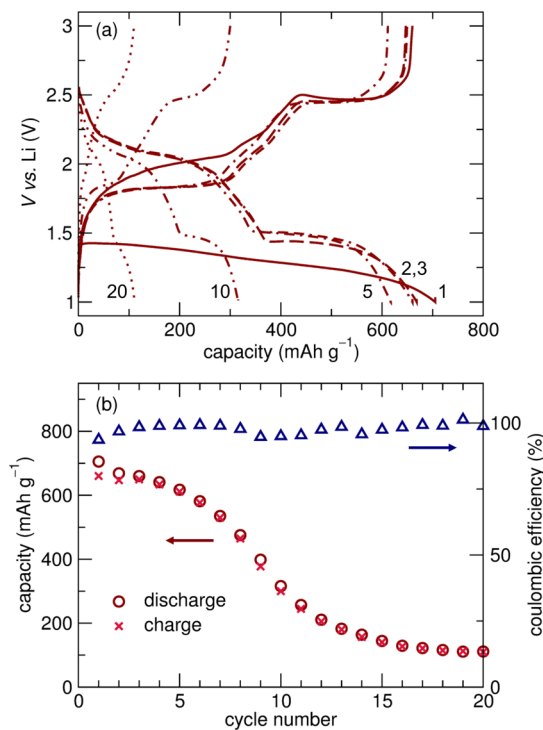


Figure 2. (a) Discharge–charge curves for FeS₂ at C/40 show good capacity retention for a conversion material over the first five cycles. Broken lines indicate later cycles, as numbered. (b) Capacity per cycle and Coulombic efficiency show surprising reversibility for the first five cycles.

or two reactions occur. This has been addressed in the previous literature, and the mechanism (one vs two reactions) appears to depend on the rate and/or temperature at which the cell is cycled.^{19,27}

It is typical for the first discharge plateau of conversion materials to occur at lower potentials than in subsequent discharges.² The higher overpotential on the first discharge is ubiquitous and has been attributed to the extra energy associated with the creation of new interfaces of the many nanoscale domains formed during the first discharge.^{4,5} There is also a contribution to the difference in potential of the first and subsequent discharges that arises from the difference in structure and composition of the first charge product from the initial material. For FeS₂ we saw a marked difference in both the potential and character of the first discharge compared to later cycling. During the first charge, there were two distinct plateaux separated by about 0.75 V. We observe a sloped region between the plateaux that contributes nearly one-third of the charge capacity. The features of the second discharge are more similar to those of the first charge than the first discharge. This is suggestive of a distinct reaction on the first discharge, which differs from subsequent cycles.

First-Principles Calculations. About 2200 Li–Fe–S structures were generated by AIRSS for the reaction of FeS₂ with 1, 1.5, 2, 3, and 4 mol of Li. While it is known that the discharge product resembles a combination of Fe and Li₂S after reacting with 4 mol of Li, treatment of multiple phases quickly becomes computationally expensive and so AIRSS calculations over the range were carried out to yield descriptions as single phase products. For the same reasons, the electrochemical curve is calculated based on the pseudobinary phase diagram (Figure 3).

The formation energies of calculated structures are plotted as a function of composition (Figure 3a). Detailed information

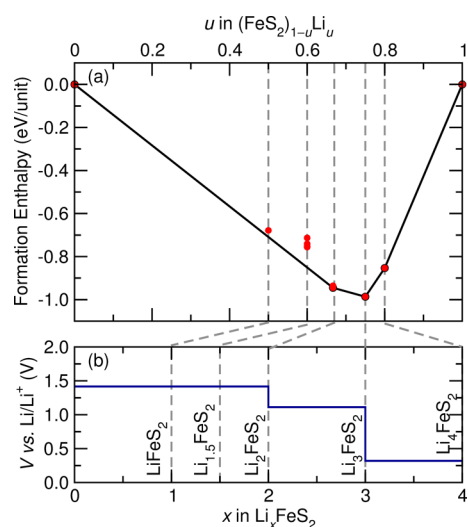


Figure 3. (a) Enthalpy per atom versus the fractional lithium concentration in the Li–FeS₂ system, simplifying the treatment of the system from a ternary to a pseudobinary. The convex hull is constructed by joining the stable structures obtained by the searches with tie lines. For further description of these phases, see Table 1. (b) On the basis of the stable phases, a prediction of the potential curve upon the first discharge involves several two-phase transformations: from FeS₂ to Li₂FeS₂, from Li₂FeS₂ to Li₃FeS₂, and finally from Li₃FeS₂ to Li₄FeS₂.

about the phases on the hull and several just above it are provided in Table 1.

Among the structures included in Table 1 are two previously published Li₂FeS₂ phases shown in Figure 1. We found the *P* $\bar{3}m1$ with octahedrally coordinated Fe (Figure 1b) to be 0.110 eV/atom above the hull. For the *P* $\bar{3}m1$ structure with sites half occupied by Li and Fe tetrahedrally coordinated by S (Figure 1c), two 1 × 2 supercells (provided in the Supporting Information) were adapted with different patterning of Li and Fe on the sites, such that each is fully occupied by one or the other. These supercells were found to have formation energies about 0.050 eV/atom above the hull. While more rigorous methods would be needed to more exactly provide the relative energies of these published phases to the hull, this would require computationally intensive efforts and have relatively low returns for this study. As such, we provide these formation energies to show that from a first pass, it is more likely that the MP or AIRSS phases, especially those in Table 2, are descriptive of the cycling products.

Tie lines connect the minimum energy structures and end members, FeS₂ and Li, to create the convex hull. The hull represents the thermodynamic equilibrium phases predicted to form as Li reacts with FeS₂ in the simplification of the ternary system to a pseudobinary. Assuming each phase transformation occurs as a two-phase reaction upon lithiation, a potential curve was calculated for the lowest energy structures (Figure 3b) using eq 5.

We were not surprised to find differences between predicted and experimental potential curves for the first discharge. We expect the plateau of the experiment to have a lower potential than was thermodynamically calculated due to the overpotential associated with kinetics of the reaction, especially the formation of many new surfaces during the nanostructuring that is well-documented for conversion materials.^{4,5} Our experimental first discharge is at only a slightly lower potential than the calculated electrochemical curve (Figure 3b). If treated as a true ternary, the combination of Fe and Li₂S would be energetically favorable to the predicted Li₄FeS₂. The predicted curve is not in agreement with second and later discharges either because, as will be discussed, the charge product is distinct from FeS₂ and so a different phase evolution occurs for the second and subsequent discharges.

Since batteries do not necessarily operate under equilibrium conditions, we considered several metastable phases near the hull. Despite variations of the relative stability, structures with similar structural motifs were near the hull for a range of Li content (1–2 mol of Li). As such, we considered structures with Li–FeS₂ ratios of 1:1, 1.5:1, and 2:1 in comparing the local structure measured by PDF to predicted structures. FeS₂ did not achieve theoretical capacity during *operando* PDF studies, so for intermediate cycling products, we considered structures with corresponding Li content. We chose to focus on those of the stoichiometry Li₃Fe₂S₄ (also referred to in the text as Li_{1.5}FeS₂), previously described in Table 1. We also calculated the relative formation energies of selected structures at this composition when relaxed with DFT+U (Table 2).

The energetics of the system do not seem to change significantly after adding the U_{eff} parameter. However, an average increase of 15% in the cell volume is observed. The increment of the lattice parameters with increasing U_{eff} value has been observed in other studies.^{38,53}

X-ray Absorption Studies. *Ex-situ* Fe K-edge XAS was carried out at various states of charge to probe the oxidation

Table 1. Description of the Experimental and Predicted Li_xFeS_2 Phases^a

stoichiometry	x in Li_xFeS_2	distance from the hull (eV/atom)	space group	structure origin	structure motif
FeS_2 ★	0	0	$P\bar{a}3$	ICSD ⁵⁰	corner-sharing octahedra
LiFeS_2	1	0.030	$P\bar{3}m1$	AIRSS	edge-sharing octahedra
$\text{Li}_3\text{Fe}_2\text{S}_4$	1.5	0.095	$P2_1$	AIRSS	edge-sharing tetrahedra
		0.097	$Pnma$	Derived from Materials Project ID:mp-768360 ⁵¹	edge-sharing tetrahedra
$\text{Li}_2\text{Fe}_2\text{S}_4$ ★	2	0.103	$P\bar{1}$	by relaxing the structure with zero magnetization	edge- and corner-sharing tetrahedra
		0.119	$Pnma$	Materials Project ID:mp-768360 ⁵¹	edge-sharing tetrahedra
		0	$P2_1/c$	Materials Project ID:mp-775931 ⁵¹	edge-sharing tetrahedra
		0.006	$P\bar{1}$	AIRSS	edge- and corner-sharing tetrahedra
		0.045	$P3m1$	ICSD, model 1 adapted ²²	layers of Li/Fe tetrahedra
		0.052	$P\bar{3}m1$	ICSD, model 2 adapted ²²	layers of Li/Fe tetrahedra
Li_3FeS_2 ★	3	0.110	$P\bar{3}m1$	ICSD ¹⁷	layers of FeS_6 octahedra
		0	$P2_1$	AIRSS	edge-sharing tetrahedra
		0	$P\bar{1}$	AIRSS	Fe–S zigzag chains
Li_4FeS_2 ★	4	0	$P\bar{1}$	AIRSS	
Li ★		0	$Im\bar{3}m$	ICSD ⁵²	

^aWe indicate with a star (★) the stable phases which are found on the convex hull. Descriptions of the structures obtained by AIRSS are presented in the Supporting Information.

Table 2. $\text{Li}_3\text{Fe}_2\text{S}_4$ Structural Formation Energies, Cell Volumes and Spin Arrangements Using GGA+ U Correction with $U_{\text{eff}} = 4$ eV

relative formation energy (meV/atom)	symmetry	volume ($\text{\AA}^3/\text{f.u.}$)	magnetic ordering	structure origin
0	$P2_1$	176.5	AFM	AIRSS
0.002	$Pnma$	178.2	FM	MP ^a
0.003	$P\bar{1}$	177.8	FM	AIRSS
0.015	$P2_1$	174.9	FM	AIRSS

^aDerived from Materials Project ID:mp-768360.⁵¹

state and coordination of Fe during the cycling of the Li– FeS_2 electrochemical system. Samples were prepared by stopping cells at a particular capacity or potential during the cycling of loose-powder Swagelok cells at $C/40$ ($Q/10$). For complex and nonequilibrium systems, such as conversion materials, *in situ* and *operando* experiments are ideal for the most representative data. However, we compared *operando* and *ex-situ* PDF for similar states of charge and saw good agreement between features of each (Figure S1), which gave us confidence in the *ex-situ* XAS. For both *ex-situ* PDF and XAS, samples were prepared just prior to experiments to minimize changes of the material between cycling and measurements. Because of extreme disorder in these materials after cycling, we focus on the near-edge energy range of the XAS data, rather than attempting to carry out an analysis of the fine structure. The discharge–charge curves for the first 1.5 cycles are shown in Figure 4a and are marked at each point a cell was stopped for an *ex-situ* measurement. The first discharge differs slightly from that shown in Figure 2a, which is due to cell-to-cell variation from the nonoptimized loose-powder cells employed. In this cell, a slight increase in potential can be seen at about 2 mol of Li; this could arise from the change in the particle size upon lithiation, as the bulk particles are broken into smaller domains.^{7,54} The XAS measured at each state of charge, and of FeS_2 as a reference, are shown for each half cycle (Figure 4b–d).

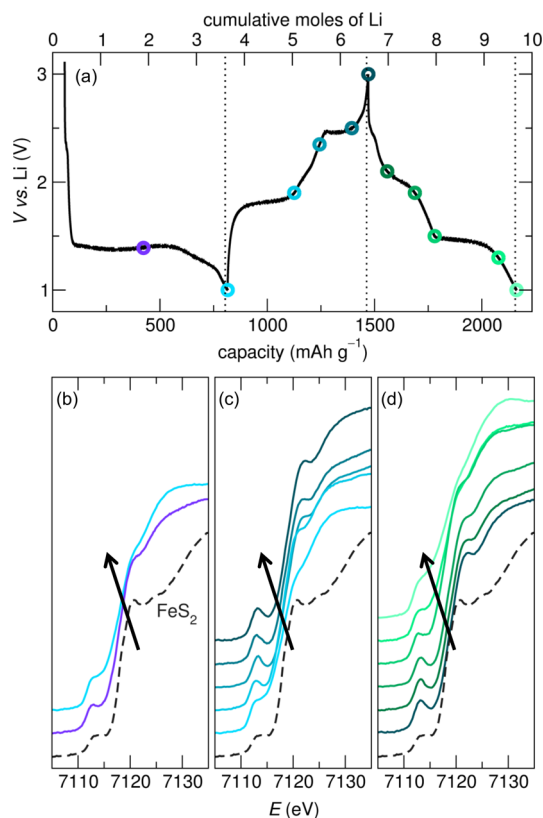


Figure 4. (a) Representative 1.5 cycles of galvanostatic cycling at $C/40$ marked at each potential or capacity at which a cell was stopped for *ex-situ* XAS. (b) The corresponding XAS for the first discharge, (c) the first charge, and (d) the second discharge. FeS_2 is plotted in each panel for reference.

During the first discharge, we observed a slight change of slope with the reduction of Fe^{2+} in FeS_2 . The product of the first discharge differed from bulk Fe (Figure S2a), which is in part due to the incomplete reaction of FeS_2 over the first

discharge. The nature of the XAS of the discharge product was also impacted by the small domain size and disorder of Fe clusters that formed with discharge. This has been observed for FeS₂ by XAS previously and will be discussed in more detail in the PDF analysis and discussion sections.

The character of the postedge, above 7.12 keV, changes from the pristine material with reduction halfway through and at the end of the first discharge (Figure 4b). Over the first charge, the slope of the edge increases with oxidation. Also, a more well-defined, sharper pre-edge peak emerges upon charging to 1.9 V (Figure 4c), just beyond the lower potential plateau (Figure 4a). This pre-edge peak grew during the rest of the charge process, over which there were relatively minor changes to the edge and postedge features (Figure 4c). The evolution of the postedge during the slope and high potential plateau of the electrochemistry could correspond to slight changes in the local coordination of Fe, for example, bond distances and bond angles.

The evolution of the XAS over the second discharge was quite different than that observed for the first discharge. Over the high potential plateau and the sloped region (above 1.5 V), the edge remained quite similar and the postedge evolved slightly (Figure 4a,d). Over the lower potential plateau, the XAS saw a more pronounced change suggestive of the reduction of Fe (Figure 4a,d). The second discharge product, similar to that of the first discharge, differed from bulk Fe (Figure S3a), likely due to small domain sizes of Fe. At these cycling conditions, there is ambiguity as to whether an intermediate phase forms on the first discharge. It has been previously reported to vary with electrolyte, temperature, rate, and particle size.^{19,26,27} The XAS of the first and second discharge products were similar and resembled small clusters of metallic Fe and, possibly, remaining FeS₂ or a ternary structure (Figure S2a).⁵⁵ Differences between the spectra of the discharge products and the bulk Fe reference are likely a consequence of small clusters of Fe and local disorder,²⁶ which we also see evidence of by *operando* PDF.

The difference of XAS evolution over the lower and higher potential plateaux of the cycling was revealing about the mechanisms at play. There was a clear conversion over the lower plateau, but relatively minor changes in the XAS at higher potentials, suggesting a different mechanism of Li reaction in this potential range, one with minimal changes to the local environment of Fe. The similarity of the XAS at higher potentials suggests the products are structurally similar. In previous work, Totir et al. interpreted the similarity of the Fe *K*-edge to mean that S redox was predominant at higher potentials.²⁴ However, a follow-up study using S *K*-edge XAS did not see clear evidence for oxidation of S to disulfide.³⁰ These studies led Totir et al. to believe that the charge product consisted of pyrrhotite (of the form Fe_xS_y) and S,³⁰ as had been proposed by other work.²⁸ We find the XAS of the charge product to be distinct from that of Fe₇S₈ (Figure S2a). In particular, the pre-edge character of XAS above the lower plateau is suggestive of tetrahedrally coordinated Fe,⁵⁶ similar to that of a cubanite (CuFe₂S₃, *F*43*m*)⁵⁷ standard (Figure S2b), in which Cu and Fe share tetrahedrally coordinated sites and Fe has an average 2.5+ oxidation state. Previous XAS studies of FeS₂ that did not see a pre-edge peak were carried out using ether-based electrolytes, in which the electrochemical behavior of S will vary.²⁷

Operando Pair Distribution Function Studies. *Operando* PDF of a cycling Li–FeS₂ cell was collected over the first 4.5

cycles (Figure S3). On the first discharge, FeS₂ reacted with Li over a single, sloping plateau near 1.5 V, yielding a capacity of 2.6 mol of Li (Figure 5a). This differs slightly from slower

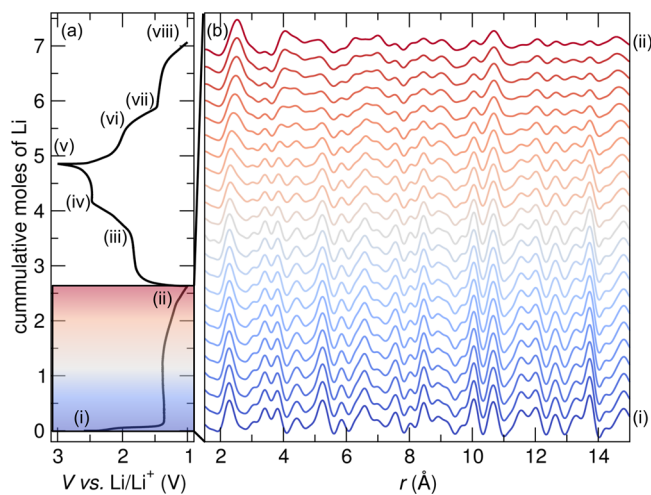


Figure 5. (a) The first 1.5 cycles of *operando* electrochemistry at $\approx C/17$. (b) The corresponding PDFs for the first discharge show conversion of (i) FeS₂ to (ii) Fe- and Li₂S-like products. The PDF also shows a decrease in crystallinity with cycling by the decreased intensity of peaks beyond 6 Å.

cycling in which it was unclear if one or two plateaux were present on the first discharge (Figure 2a). The general behavior and features of the discharge–charge curves of the *operando* cell were similar to those seen in the cycling of loose-powder Swagelok cells.

Over the first discharge, *operando* PDF shows a change in local structure from FeS₂ to Fe- and Li₂S-like domains (Figure 5b). PCA was carried out to discern if intermediate local structures evolved during the first discharge. By PCA and linear combination transformations to satisfy criteria, as described by Chapman et al.,⁴⁹ we determined three significant PCs. The first PC is FeS₂ and matches the pattern before cycling (Figure 5b,i). The second PC is representative of the product of the first discharge, which resembles Fe and Li₂S (Figure 5b,ii). The third PC forms intermediately and is then consumed. This third PC does not resemble the ternary local structures observed in later cycles but does have some features in common with the product of the fifth discharge. The PCs and the percentages in which they appear over the first discharge can be found in Figures S4 and S5, respectively. For the discharge product, the intensity of peaks at even 14 Å was low, indicating poor long-range order, as is expected for conversion materials.^{4,5} Further analysis of the discharge product will be discussed in the following sections.

The first charge took place over two plateaux and a sloped region between them and achieved a charge capacity of about 2.3 mol of Li (Figure 6). The first plateau (Figure 6a,ii to iii), near 1.9 V, contributed 1 mol of Li to the capacity and the second (Figure 6a, iv to v), at about 2.5 V, contributed 0.7 mol of Li. Between them, the sloped region (Figure 6a, iii to iv) contributed a non-negligible 0.6 mol of Li. Over the first charge, there was a conversion from the Fe- and Li₂S-like domains (Figure 6c, ii) to another local structure (Figure 6c,v) distinct from both FeS₂ (Figure 6b,i) and the first discharge product (Figure 6b,ii). Above the lower plateau (Figure 6a,iii to v), the first three major peaks between 1.5 and 5 Å, shifted to

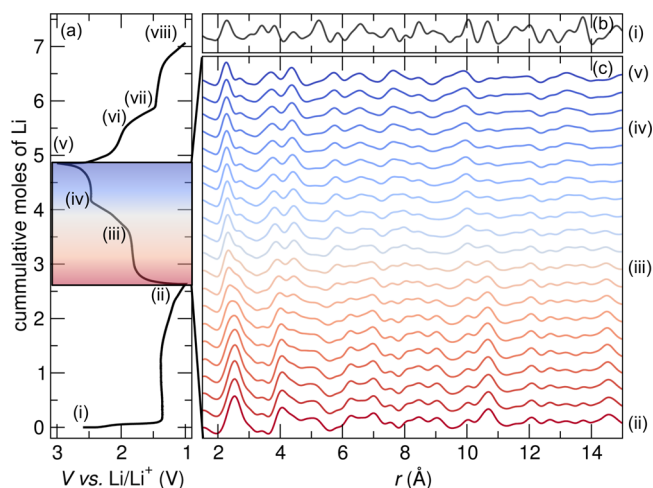


Figure 6. (a) First 1.5 cycles of *operando* electrochemistry at $\approx C/17$. (b) PDF of the FeS_2 before cycling. (c) The PDFs for the first charge show conversion of (ii) discharge products (Fe- and Li_2S -like domains) to (iii) an intermediate phase and then (iii) to (iv) the shifting of pairwise interactions to lower r over the sloped region and (iv) the high potential plateau with continued charging. The local structure shows that (c,v) the charge product has much less long-range order and is not FeS_2 (b,i).

lower r . As was observed for the first discharge product, the higher r peaks decreased in intensity, indicating a decrease in long-range order.

We found electrochemical features during the second discharge similar to those of the first charge, with plateaux near 2 V (Figure 7a,v to vi) and 1.5 V (Figure 7a, vii to viii) and a total discharge capacity of about 2.2 mol of Li. During the second discharge, the local structure initially evolved with the shifting of low and moderate r peaks to higher r (Figure 7b,v to vii), followed by a change of the local structure to resemble the first discharge product (Figure 7b,vii to viii).

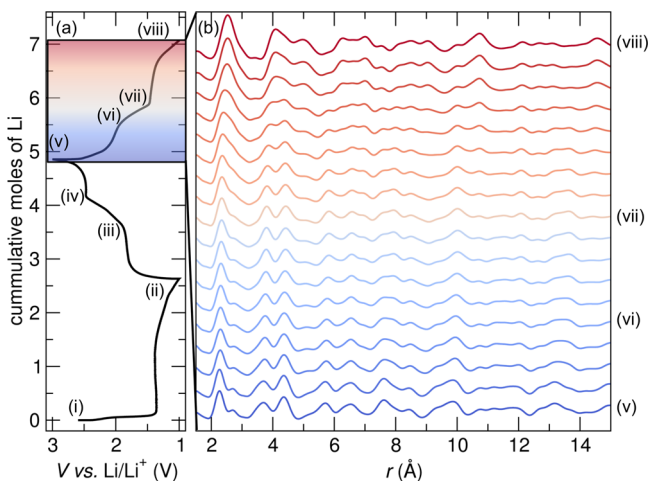


Figure 7. (a) First 1.5 cycles of *operando* electrochemistry at $\approx C/17$. (b) The corresponding PDFs for the second discharge suggest a similar mechanism as the first charge, which is distinct from the first discharge. (v to vi) Over the high potential plateau and (vi to vii) the sloped region, there is an increase in the pairwise interaction lengths with reduction, an expansion of the local structure, suggestive of Li insertion into a host structure. (vii to viii) Over the low-potential plateau, at about 1.5 V, there is a conversion to (viii) Fe- and Li_2S -like products, similar to (Figure 5b,ii) the products of the first discharge.

Considering the first 1.5 cycles of *operando* PDF together, a few key observations can be made. Similar to XAS, PDF showed that the discharge products locally resembled Fe and Li_2S (Figure 5b,ii and Figure 7b,viii) and that FeS_2 (Figure 5b,i) was not recovered on charge (Figure 6b,v). The shifting of peaks during the first charge and second discharge (as well as during subsequent cycles) suggests the charge product is structurally similar to an intermediate. This is in line with the minor changes of the postedge of XAS in this regime of potential and Li content. In the high potential regime of the second discharge, we propose there is some storage of Li by a host structure by an insertion-extraction mechanism at lower Li content, followed by conversion to Fe- and Li_2S -like domains at higher Li content and lower potentials. Further analysis of discharge, charge, and intermediate products are discussed in greater detail following.

Pair Distribution Function Analysis of Intermediate Ternary Products. Several structures have been proposed to form during the cycling of FeS_2 . Among those are phases hypothesized to accommodate a range of Li content and, accordingly, store charge by a Li insertion-extraction mechanism at high potentials and low Li content. We also see evidence for this mechanism in our study. By the analysis of *operando* PDF, we elucidate new information about the local structure of the ternary intermediate and a related charge product.

Among the calculated and published ternary Li–Fe–S phases we considered, there were a number of local structural motifs present. At the smallest correlation distance, we saw a difference of Fe octahedrally or tetrahedrally coordinated by S in the simulated PDF. Fits to intermediate cycling products (collected at 1.56 V and 1.3 mol of Li, along the sloped region of the second discharge) show that published Li_2FeS_2 with FeS_6 octahedra¹⁷ does not capture the features of the measured PDF as well as structures with FeS_4 tetrahedra (Figure S6). This is consistent with the pre-edge peak in XAS at these potentials, which is indicative of tetrahedrally coordinated Fe (Figure 4).

To analyze the PDF of the intermediate and related charge products of cycling, we focused on PDF measured over the sloped region of the second discharge at 1.74 V with about 1.2 mol of Li. Since the full capacity was not achieved and calculated structures at various compositions had similar local motifs, we considered several metastable calculated phases at the composition $\text{Li}_{1.5}\text{FeS}_2$ with FeS_4 tetrahedra (Figure 8). The metastable $\text{Li}_{1.5}\text{FeS}_2$ structures considered generally consist of Li between 1D or quasi-1D chains of FeS_4 tetrahedra, each with a unique local motif beyond the first coordination shell. The $P\bar{1}$ structure (Figure 8a) consists of disrupted corrugated chains, which meet to form a group of four corner-sharing tetrahedra, referred to hereafter as a “tetrad” motif (Figure 9i) (GGA+U structure used, see Table 2). The $P2_1$ structure (Figure 8b) has edge-sharing FeS_4 tetrahedra that arrange as corrugated chains (Figure 9ii), with Li between them (by PBE, see Table 2). The $Pnma$ phase (Figure 8c) has linear chains of edge-sharing FeS_4 tetrahedra (Figure 9iii) (derived from Materials Project,⁵¹ relaxed by PBE, see Table 2). Among the other calculated structures with tetrahedrally coordinated Fe, each had one of these three motifs.

We fit the three representative structures shown in Figure 8 to an intermediate product along the slope of the second discharge at 1.74 V and 1.2 mol of Li. The data was fit between 1.5 and 5.5 Å and lattice parameters, nonspecial angles, a correlated motion parameter (δ_{Li} in PDFgui), and the

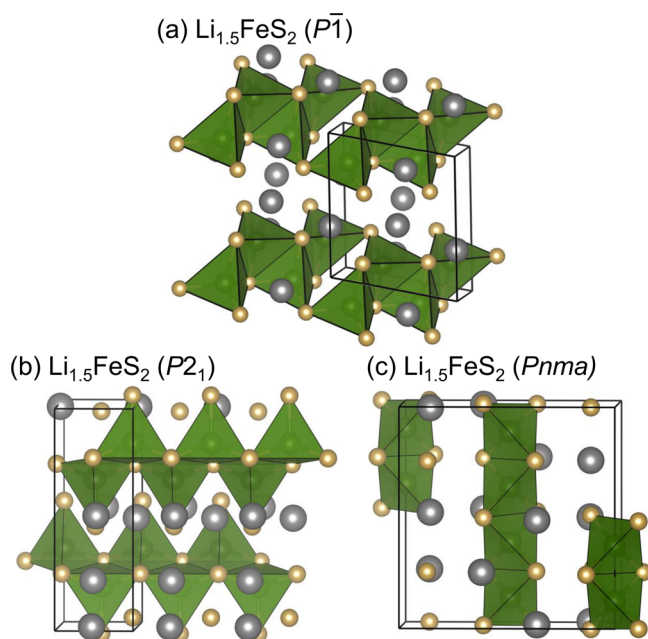


Figure 8. Several structures with the composition $\text{Li}_{1.5}\text{FeS}_2$ with tetrahedrally coordinated Fe from AIRSS calculations. (a) $\text{Li}_{1.5}\text{FeS}_2$ with $P\bar{1}$ symmetry has both edge- and corner-sharing FeS_4 tetrahedra (GGA+ U). (b) $\text{Li}_{1.5}\text{FeS}_2$ with $P2_1$ symmetry has corrugated chains of edge-sharing tetrahedra (PBE), and (c) $\text{Li}_{1.5}\text{FeS}_2$ with $Pnma$ symmetry has linear chains of edge-sharing tetrahedra (derived from Materials Project, relaxed by PBE).

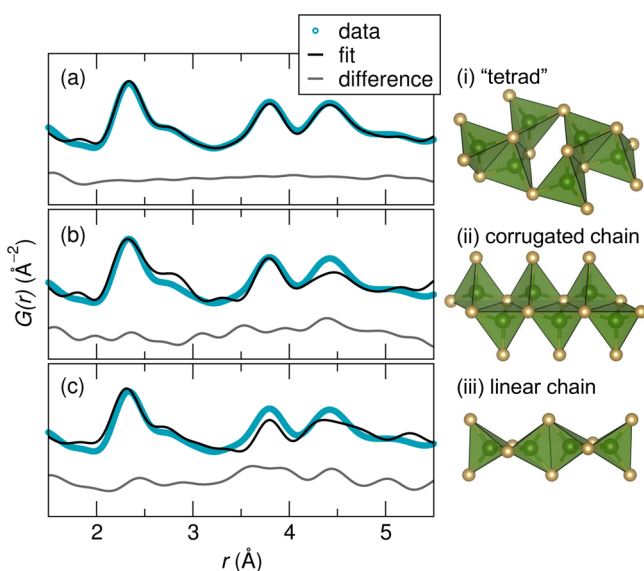


Figure 9. Fits of three calculated structures with the composition $\text{Li}_{1.5}\text{FeS}_2$ with tetrahedrally coordinated Fe to data collected at 1.74 V and 1.2 mol of Li during the second discharge and various local structure motifs. (a) $\text{Li}_{1.5}\text{FeS}_2$ with $P\bar{1}$ symmetry has both edge- and corner-sharing FeS_4 tetrahedra, which we refer to as (i) a "tetrad". (b) $\text{Li}_{1.5}\text{FeS}_2$ with $P2_1$ symmetry has (ii) corrugated chains of edge-sharing tetrahedra. (c) $\text{Li}_{1.5}\text{FeS}_2$ with $Pnma$ symmetry has (iii) linear chains of edge-sharing tetrahedra.

U_{iso} of each atom were refined in a single-phase fit with a nanoparticle size (the parameter spdiameter in PDFgui) of 40 Å. It is important to note that the "tetrad" phase has the more complex local structure and the lowest symmetry; this enables refinement of more Fe–Fe correlation distances and

parameters that contribute to the goodness of fit of this local motif to measured PDF.

Fitting over this small range, on the same length scale of the structural motifs, gave good fits with small difference curves (Figure 9). While the corrugated and linear chains (Figure 9ii,iii) fit the local structure quite well (Figure 9b,c), there are still several correlations not completely captured by these motifs. Both the fit and the nature of the difference curve show the tetrad structural motif (in the $P\bar{1}$ phase) best models the local structure of the measured PDF (Figure 9i,a). The low symmetry of the $P\bar{1}$ structure and the corresponding larger number of refined parameters undoubtedly contribute to the goodness of fit to the measured data. This structure also has the most variety of connectivity, with both edge- and corner-sharing tetrahedra, which enables it to fit the local structure. When refined to higher r , the overall quality of fit decreases, which suggests the local and average structures are different. In particular, it appears that the local structure resembles the local motifs described by the calculated phases, but there is insufficient correlation of these units to give a periodic structure. We carried out fits to the three published structures (shown in Figure 1 and described above) with similar fitting conditions as the calculated structures and less satisfactory fits (Figure S7).

Of the local structures considered, the tetrad motif present in the $\text{Li}_{1.5}\text{FeS}_2$ with $P\bar{1}$ symmetry gave the best local fit. Accordingly, this is a possible structural unit in the intermediate products. However, there could be a variety of local motifs contributing to the measured PDF. From PDF and XAS, we know the local structure of the intermediate and charge products are similar. By fitting the $P\bar{1}$ structure to 15 Å at various states of charge above the lower potential plateau, on both the first charge and second discharge, we see many of the features are captured (Figures S8 and S9). It is important to note that the average structure is not well-defined by the $P\bar{1}$, or any other, of the phases we considered; when we extend the good local fit for the tetrad motif to even 15 Å, the overall fit is not as good (Figure S8).

Pair Distribution Function Analysis of Discharge Products. By XAS,^{24,25,54} transmission electron microscopy,^{4,5,58} and ²⁶Fe Mössbauer,²⁶ among other methods, researchers have previously found that the metal formed during the discharge of conversion electrodes tends to occur as disordered clusters of metal atoms on the order of 10 Å to 50 Å in diameter. Deviations of the structure of nanoparticles from the bulk structure has been observed for several systems, including gold nanoparticles.⁵⁹

As previously mentioned, for FeS_2 the first and second discharge products locally resembled Fe and Li_2S . Upon a closer look we found equilibrium body-centered cubic (*bcc*) Fe did not fully capture the local structure of the first discharge product (Figure S10), which has been previously observed for other Fe-based conversion electrode materials.^{11,13} Comparing the PDF of the first discharge product to a two-phase fit of Li_2S and *bcc* Fe, *bcc* Fe contributes an extra peak at 5.6 Å and does not capture the peaks at 6.3 and 8.7 Å (Figure S10). From similar comparisons to the local structure of face-centered cubic and body-centered tetragonal Fe, we found these local structures were not a good match to the measured PDF. We also compared the local structure of the first discharge to hexagonal close-packed (*hcp*) Fe, which was close, but like *bcc* Fe had extra or missing peaks (Figure S10); *hcp* Fe captured

the peaks at 6.3 and 8.7 Å that *bcc* Fe was missing but had extra features at 3.6 and 5.6 Å.

To better model the local structure, we employed a supercell of *bcc* Fe whose atomic positions were perturbed from their ideal sites, using the RMCProfile software suite.⁶⁰ A $3 \times 3 \times 3$ supercell of 54 atoms was generated from a single unit cell of *Im* $\bar{3}m$ (*bcc*) Fe with Fe in the 2a Wyckoff site at (0,0,0). Atoms were allowed to translate a maximum of 0.01 Å per move, and a minimum approach distance of 2.46 Å was applied, employing approximately 5×10^6 Monte Carlo moves. The relaxation yielded a local structure that offered a good compromise between *bcc* and *hcp* Fe (Figure S10). The structure produced by the simulation was then used in a two phase fit of the discharge product with Li_2S as the second phase. In combination with Li_2S , the disordered Fe, with an approximate cluster diameter of 10 Å to 12 Å (set as *spdiameter* in PDFgui⁴⁸), captures the dominant features of the first discharge product in the range of 1.5 Å to 15 Å (Figure 10a). We know

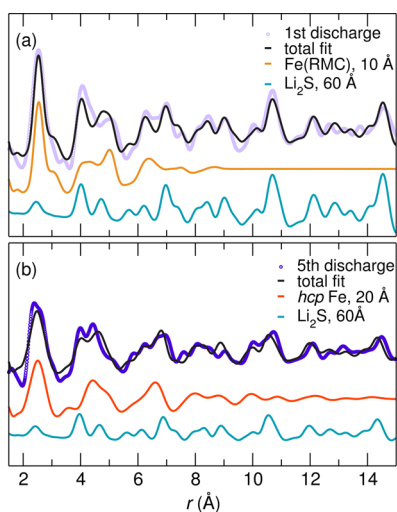


Figure 10. (a) Two-phase fit of the first discharge and contributions from each phase: disordered Fe from the relaxation of a *bcc* Fe supercell with a particle diameter of 10 Å and Li_2S with a particle diameter of 60 Å. (b) Two-phase fit of the fifth discharge and contributions from each phase: *hcp* Fe with a particle diameter of 20 Å and Li_2S with a particle diameter of 60 Å.

from previous work that the diameter of a particle or cluster will relate to the damping of the signal from that material in the PDF.⁵⁹ For these fits, the lattice parameters and U_{iso} of all atoms were refined. Visualization of the initial *bcc* Fe supercell and the disordered Fe structures are available in Figure S11.

The local structure of the first, second, and third discharge products were similar (Figure 11a), and can therefore be described by clusters of disordered Fe and Li_2S . The PDF of the fourth and fifth discharge products were different than the previous and better described as a combination of *hcp* Fe and Li_2S . A two-phase fit of the fifth discharge product with about 20 Å diameter clusters of *hcp* Fe and Li_2S model the local structure well (Figure 10b). This analysis of the discharge products does not preclude other species that may be present in small amounts.

It appears that Fe clusters grow with subsequent discharges, possibly as the crystallinity of the system decreases with each cycle, which could enable increased Fe diffusion. Despite the evolution of the discharge product with cycling, there are only

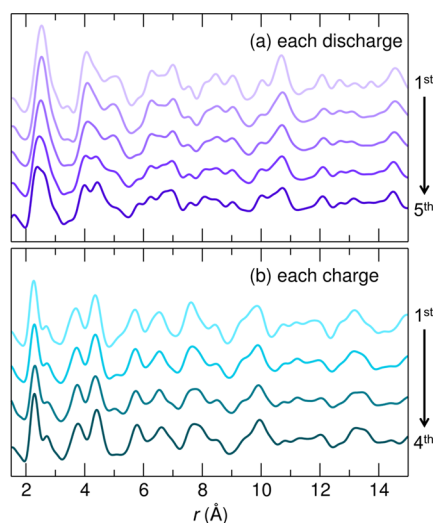


Figure 11. (a) PDFs of the first through fifth discharges of FeS_2 show changes in the local structure with cycling. The first through the third discharge products are similar, corresponding to clusters of disordered Fe and Li_2S locally. The fourth and fifth discharge products have a different local structure, better matched to small clusters of *hcp* Fe and Li_2S . The fits of the first and fifth discharge products can be found in Figure 10. (b) PDFs of the first through fourth charge products show similar local structures.

minor changes to the charge product (Figure 11a). Despite the apparent growth of clusters and their resemblance to *hcp* Fe at discharge in later cycles, the cluster formation appears to be mostly reversible, as no major changes are evident in the four charge products over which PDF was collected (Figure 11b).

DISCUSSION

By a combination of first-principles calculations, *operando* PDF, and *ex-situ* XAS, we bring new insight into the local structure evolution at the cathode in Li– FeS_2 cells. We make a point of examining later cycles in addition to the first discharge to understand the processes most representative of the system. In the cycling of micron-sized particles of FeS_2 at room temperature at C/17 in carbonate electrolyte, we observed conversion to Fe- and Li_2S -like domains during the first discharge by *operando* PDF. On the first charge we observed a conversion from Fe and Li_2S to an intermediate, ternary local structure over the lower potential plateau. With continued oxidation, the low *r* peaks shift, rather than forming a new local structure. The shift of these peaks with oxidation and reduction corresponds to the expansion and contraction of bond lengths and, consequently, cell parameters with cycling, suggestive of a Li insertion-extraction mechanism (similar to the intercalation of Li for $\text{Li}_{1-x}\text{CoO}_2$) above the lower potential plateau between the ternary intermediate and a related charge product. *Ex-situ* Fe *K*-edge XAS also shows only minor changes above the lower potential plateau. An insertion-extraction regime has been proposed in previous reports and our *operando* PDF enables visualization of this mechanism.

The combination of *operando* PDF and *ex-situ* XAS also allows us to expand upon hypothesized phases to describe the intermediate, ternary local structure, and the related charge product. The pre-edge feature in Fe *K*-edge XAS and the first correlation peak in PDF indicate an intermediate product with tetrahedrally coordinated Fe. The tetrahedral features persist in both the PDF and XAS for all electrochemistry above the lower

potential plateau. The combination of this data is in contrast to previous literature that suggests octahedral coordination of Fe by S, either in ternary phases or in off-stoichiometry Fe_xS_y pyrrhotite.^{27,28,30} However, pyrrhotite has primarily been reported for ether-based electrolytes, in which S electrochemistry and solubility are known to differ and could impact the structural evolution. For our study in a carbonate-based electrolyte solution, we see a poor fit of phases with FeS_6 octahedra to our data (Figure S6).

There are previously proposed ternary phases with FeS_4 tetrahedra (Figure 1c,d); however, we found the local structure of these phases beyond the first coordination shell were not a good fit to measured PDF (Figure S7).^{22,23} To further explore the local structure, AIRSS was employed to predict a library of ternary structures with various local motifs. We found reasonably good fits for those motifs with linear or corrugated chains of edge-sharing FeS_4 tetrahedra at intermediate states of charge. The best local fit, however, was for a “tetrad” motif, which has both edge- and corner-sharing FeS_4 tetrahedra. All three motifs capture most of the local features of the intermediate PDF well, but none have great agreement to the average structure, indicating there is poor correlation at higher r . It is well-known that conversion systems lack long-range order, making our findings consistent with previous reports on conversion systems.^{5–7}

The collection and analysis of PDF over 4.5 cycles allows a unique opportunity to relate structure and performance. We see over the five discharge products an increase in the size of Fe clusters, modeled in fits as spdiameter . As the clusters grow, there is also a change from disordered Fe to a local structure resembling *hcp* Fe. The larger diameter could enable the lower energy, more ordered Fe structure. Previous studies suggest that Fe-based conversion systems show favorable reversibility relative to Cu-based analogues due in part to the smaller size of Fe particles formed, with the cluster size limited by the diffusivity of the metal during discharge.⁵ The combination of small-angle X-ray scattering and PDF has been previously employed by Wiaderek et al. to reveal a dependence of cluster size on anion chemistry for Fe-based conversion electrodes, with fluorides forming larger particles than oxides (35 Å compared to 20 Å).¹³ For FeS_2 , we find Fe clusters for the first discharge on the order of 10 Å in diameter. Combining the results of the study by Wiaderek et al. with this one,¹³ it is possible that nanoparticle size varies with anion electronegativity. However, it is unclear if this trend is exclusively applicable to Fe-based materials or is more general. Other factors, such as the degree of ionicity or covalency of bonds, could be at play in the impact of anion chemistry on metal cluster size. Despite the evolution in the discharge products, the first four charge products remain quite similar, even as the charge capacity fades slightly. *Operando* PDF at later cycles could further inform failure mechanisms for this system.

The intriguing difference between FeS_2 and a number of other conversion systems is the dual modes of storage. FeF_2 ,⁴ MnO ,⁷ CuF_2 ,⁸ and many others store Li by a single conversion step. In isostructural pyrite CoS_2 , which does have multiple reactions, the observed intermediate products are a combination of Li_2S and Co–S binaries.⁶¹ We present here strong evidence that the cathode of an Li– FeS_2 cell operates by two different mechanisms beyond the first discharge under cycling conditions similar to those employed here. At slower rates or higher temperature, the first discharge can involve an

intermediate product, but this would be two conversion steps, rather than the pairing of insertion-extraction and conversion reactions. The combination of insertion-extraction and conversion seen in the second and subsequent cycles of FeS_2 system are similar to observations for VS_4 , which on charge undergoes conversion from V clusters and Li_2S to a ternary $\text{Li}_{3+x}\text{VS}_4$ structure that is stable over a range of Li content, and so then undergoes an insertion-extraction mechanism from the host structure at higher potentials.⁹ The reversible behavior of FeS_2 could arise from the two types of charge storage mechanisms that occur.

CONCLUSIONS

This examination of the Li– FeS_2 secondary energy storage system provides new insights into the previously studied cycling mechanism at slow rates, room temperature, and in a carbonate-based electrolyte by *operando* PDF and *ex-situ* *K*-edge XAS. During the first discharge, FeS_2 undergoes conversion to Fe- and Li_2S -like domains under these cycling conditions. Initially, the Fe clusters are disordered, not quite resembling *bcc* or *hcp* Fe. In continued cycling, the Fe clusters grow and the local structure more closely resembles *hcp* Fe, possibly stabilized by the growth of metal clusters.

The first charge product is not FeS_2 , and consequently, the second discharge follows a different evolution of local structure than the first. The first charge occurs as two steps: (i) conversion between Fe and Li_2S and a ternary intermediate over the lower plateau and (ii) an insertion-extraction reaction with a host structure over the higher potential slope and plateau. The Li insertion-extraction is evidenced in the PDF by the shifting of low r peaks in real space, corresponding to expansion/contraction of the structure as bond lengths increase/decrease with reduction/oxidation. The related intermediate and charge products have tetrahedrally coordinated Fe. We suggest several structures with local motifs that capture the low r features of the measured PDF well and describe the local structure of the intermediate cycling products. The second discharge appears to follow the same steps as the first charge in the reverse order. We hypothesize that the hybrid modes of storage, insertion/extraction and conversion, could be important in identifying promising candidates for next-generation, high capacity electrode materials.

In addition to our contribution to the understanding of FeS_2 as a conversion electrode, we also show effective methodology for investigating dynamic and disordered systems, including conversion reaction electrode candidates. We especially highlight the utility of combined computational and local structure methods. Further, we show that the application of *operando* methods and structural characterization well beyond the first discharge reveal useful insight into the mechanisms of charge storage and even cell failure. This work also contributes to the literature on conversion electrodes by characterizing the mechanisms of a relatively reversible system. Mechanistic studies with advanced characterization methods permit the identification of general rules for more reversible candidates, toward realizing the promise of conversion reaction systems for electrochemical energy storage.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00070.

Further cycling of *operando* PDF, a comparison of *operando* and *ex-situ* PDF at similar states of charge, Fe K-edge XAS of several standards, additional fits of measured PDF to published phases and with higher *r* refinements, and descriptions of calculated structures (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: mbutala@umail.ucsb.edu.

*E-mail: ajm255@cam.ac.uk.

*E-mail: cpg27@cam.ac.uk.

*E-mail: seshadri@mrl.ucsb.edu.

ORCID 

Martin Mayo: 0000-0001-5761-6736

Vicky V. T. Doan-Nguyen: 0000-0003-4204-3271

Geneva Laurita: 0000-0001-9577-150X

Ram Seshadri: 0000-0001-5858-4027

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.M.B. acknowledges support by the Fletcher Jones and Peter J. Frenkel Foundation Fellowships. V.V.T.D.-N. is supported by the University of California President's Postdoctoral Fellowship and the UCSB California NanoSystems Institute Elings Prize Fellowship. V.V.T.D.-N. gratefully acknowledges the Southern California Electrochemical Energy Storage Alliance (SCEESA), supported by the UCSB CNSI. Experiments at UCSB made use of MRL facilities, supported by the MRSEC Program of the NSF under Grant No. NSF-DMR 1121053. M.A.L. was supported by the RISE program through Grant No. NSF-DMR 1121053. This work was partially supported by the IMI Program of the National Science Foundation under Award No. DMR 08-43934. M.M. and A.J.M. acknowledge the support from the Winton Programme for the Physics of Sustainability. C.P.G. and S.B. thank EPSRC for financial support. This research made use of resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. X-ray absorption experiments were performed at APS 20-BM-B under GUP-41555. Sector 20 operations are supported by the U.S. DOE and the Canadian Light Source. X-ray scattering experiments were performed at APS 11-ID-B under GUP-42128 and GUP-45245. The authors also thank Professor Anton Van der Ven for helpful discussions.

■ REFERENCES

- (1) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22*, 587–603.
- (2) Cabana, J.; Monconduit, L.; Larcher, D.; Palacin, M. R. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions. *Adv. Mater.* **2010**, *22*, E170–E192.

- (3) Hayner, C. M.; Zhao, X.; Kung, H. H. Materials for Rechargeable Lithium-Ion Batteries. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 445–471.

- (4) Wang, F.; et al. Conversion Reaction Mechanisms in Lithium Ion Batteries: Study of the Binary Metal Fluoride Electrodes. *J. Am. Chem. Soc.* **2011**, *133*, 18828–18836.

- (5) Wang, F.; Yu, H.-C.; Van der Ven, A.; Thornton, K.; Pereira, N.; Zhu, Y.; Amatucci, G. G.; Graetz, J. Ionic and Electronic Transport in Metal Fluoride Conversion Electrodes. *ECS Trans.* **2013**, *50*, 19–25.

- (6) Lowe, M. A.; Gao, J.; Abruña, H. D. In *Operando X-ray Studies of the Conversion Reaction in Mn₃O₄ Lithium Battery Anodes*. *J. Mater. Chem. A* **2013**, *1*, 2094–2103.

- (7) Butala, M. M.; Danks, K. R.; Lumley, M. A.; Zhou, S.; Melot, B. C.; Seshadri, R. MnO Conversion in Li-ion Batteries: In situ Studies and the Role of Messtructuring. *ACS Appl. Mater. Interfaces* **2016**, *8*, 6496–6503.

- (8) Hua, X.; Robert, R.; Du, L.-S.; Wiaderek, K. M.; Leskes, M.; Chapman, K. W.; Chupas, P. J.; Grey, C. P. Comprehensive Study of the CuF₂ Conversion Reaction Mechanism in a Lithium Ion Battery. *J. Phys. Chem. C* **2014**, *118*, 15169–15184.

- (9) Britto, S.; Leskes, M.; Hua, X.; Hébert, C.-A.; Shin, H. S.; Clarke, S.; Borkiewicz, O.; Chapman, K. W.; Seshadri, R.; Cho, J.; Grey, C. P. Multiple Redox Modes in the Reversible Lithiation of High-Capacity, Peierls-Distorted Vanadium Sulfide. *J. Am. Chem. Soc.* **2015**, *137*, 8499–8508.

- (10) Doan-Nguyen, V. V. T.; et al. Molybdenum Polysulfide Chalcogenides as High-Capacity, Anion-Redox-Driven Electrode Materials for Li-Ion Batteries. *Chem. Mater.* **2016**, *28*, 8357–8365.

- (11) Shyam, B.; Chapman, K. W.; Balasubramanian, M.; Klingler, R. J.; Srajer, G.; Chupas, P. J. Structural and Mechanistic Revelations on an Iron Conversion Reaction from Pair Distribution Function Analysis. *Angew. Chem., Int. Ed.* **2012**, *51*, 4852–4855.

- (12) Wiaderek, K. M.; Borkiewicz, O. J.; Castillo-Martinez, E.; Roberts, R.; Pereira, N.; Amatucci, G. G.; Grey, C. P.; Chupas, P. J.; Chapman, K. W. Comprehensive Insights into the Structural and Chemical Changes in Mixed-Anion FeOF Electrodes by Using Operando PDF and NMR Spectroscopy. *J. Am. Chem. Soc.* **2013**, *135*, 4070–4078.

- (13) Wiaderek, K. M.; Borkiewicz, O. J.; Pereira, N.; Ilavsky, J.; Amatucci, G. G.; Chupas, P. J.; Chapman, K. W. Mesoscale Effects in Electrochemical Conversion: Coupling of Chemistry to Atomic- and Nanoscale Structure in Iron-Based Electrodes. *J. Am. Chem. Soc.* **2014**, *136*, 6211–6214.

- (14) Preto, S. K.; Tomczuk, Z.; von Winbush, S.; Roche, M. R. Reactions of FeS₂, CoS₂, and NiS₂ Electrodes in Moleten LiCl–KCl Electrolytes. *J. Electrochem. Soc.* **1983**, *130*, 264–273.

- (15) Masset, P. J.; Guidotti, R. A. Thermal Activated (“Thermal”) Battery Technology Part IIIa: FeS₂ Cathode Material. *J. Power Sources* **2008**, *177*, 595–609.

- (16) Brec, R.; Dugast, A.; le Mehaute, A. Chemical and Electrochemical Study of the Li_xFeS₂ Cathodic System (0 < x ≤ 2). *Mater. Res. Bull.* **1980**, *15*, 619–625.

- (17) Le Mehaute, A.; Brec, R.; Dugast, A.; Rouxel, J. The Li_xFeS₂ Electrochemical System. *Solid State Ionics* **1981**, *3–4*, 185–189.

- (18) Shao-Horn, Y.; Osmialowski, S.; Horn, Q. C. Nano-FeS₂ for Commercial Li/FeS₂ Primary Batteries. *J. Electrochem. Soc.* **2002**, *149*, A1499–A1502.

- (19) Shao-Horn, Y.; Osmialowski, S.; Horn, Q. C. Reinvestigation of Lithium Reaction Mechanism in FeS₂ Pyrite at Ambient Temperature. *J. Electrochem. Soc.* **2002**, *149*, A1547–A1555.

- (20) Yersak, T. A.; Macpherson, H. A.; Kim, S. C.; Le, V.-D.; Kang, C. S.; Son, S.-B.; Kim, Y.-H.; Trevey, J. E.; Oh, K. H.; Stoldt, C.; Lee, S.-H. Solid State Enabled Reversible Four Electron Storage. *Adv. Energy Mater.* **2013**, *3*, 120–127.

- (21) Evans, T.; Piper, D. M.; Kim, S. C.; Han, S. S.; Bhat, V.; Oh, K. H.; Lee, S.-H. Ionic Liquid Enabled FeS₂ for High-Energy-Density Lithium-Ion Batteries. *Adv. Mater.* **2014**, *26*, 7386–7392.

- (22) Batchelor, R. J.; Einstein, F. W. B.; Jones, C. H. W.; Fong, R.; Dahn, J. R. Crystal Structure of Li_2FeS_2 . *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 3699–3702.
- (23) Blandeau, L.; Ouvrard, G.; Calage, Y.; Brec, R.; Rouxel, J. Transition-metal Dichalcogenides from Disintercalation Process. Crystal Structure Determination and Mössbauer Study of Li_2FeS_2 and its Disintercalates Li_xFeS_2 ($0.2 \leq x \leq 2$). *J. Phys. C: Solid State Phys.* **1987**, *20*, 4271–4281.
- (24) Totir, D. A.; Bae, I. T.; Hu, Y.; Antonio, M. R.; Stan, M. A.; Scherson, D. A. In Situ Fe K-Edge X-ray Absorption Fine Structure of a Pyrite Electrode in a Li/Polyethylene Oxide(LiClO_4)/ FeS_2 Battery Environment. *J. Phys. Chem. B* **1997**, *101*, 9751–9756.
- (25) Strauss, E.; Calvin, S.; Mehta, H.; Golodnitsky, D.; Greenbaum, S. G.; denBoer, M. L.; Dusheiko, V.; Peled, E. X-ray Absorption Spectroscopy of Highly Cycled Li/Composite Polymer Electrolyte/ FeS_2 Cells. *Solid State Ionics* **2003**, *164*, 51–63.
- (26) Jones, C. H. W.; Kovacs, P. E.; Sharma, R. D.; McMillan, R. S. Iron-57 Mössbauer Spectroscopy of Reduced Cathodes in the Lithium/Iron Disulfide Battery System: Evidence for Superparamagnetism. *J. Phys. Chem.* **1990**, *94*, 832–836.
- (27) Tryk, D. A.; Kim, S.; Scherson, W. X. D. A.; Antonio, M. R.; Leger, V. Z.; Blomgren, G. E. Electrochemical Insertion of Lithium into Pyrite from Nonaqueous Electrolytes at Room Temperature: An *in situ* Fe K-Edge X-ray Absorption Fine Structure Study. *J. Phys. Chem.* **1995**, *99*, 3732–3735.
- (28) Fong, R.; Jones, C. H. W.; Dahn, J. R. A Study of Pyrite-Based Cathodes for Ambient Temperature Lithium Batteries by *In Situ* ^{57}Fe Mössbauer Spectroscopy. *J. Power Sources* **1989**, *26*, 333–339.
- (29) Fong, R.; Dahn, J. R.; Jones, C. H. W. Electrochemistry of Pyrite-Based Cathodes for Ambient Temperature Lithium Batteries. *J. Electrochem. Soc.* **1989**, *136*, 3206–3210.
- (30) Totir, D. A.; Antonio, M. R.; Schilling, P.; Tittsworth, R.; Scherson, D. A. In Situ Sulfur K-Edge X-ray Absorption Near Edge Structure of an Embedded Pyrite Particle Electrode in a Non-Aqueous Li^+ -Based Electrolyte Solution. *Electrochim. Acta* **2002**, *47*, 3195–3200.
- (31) Gard, P.; Sourisseau, C.; Ouvrard, G.; Brec, R. Infrared Study of Lithium Intercalated Phases in the Li_xFeS_2 System ($0 \leq x \leq 2$). Characterization of a New Iron Disulfide. *Solid State Ionics* **1986**, *20*, 231–238.
- (32) Pickard, C. J.; Needs, R. J. High-Pressure Phases of Silane. *Phys. Rev. Lett.* **2006**, *97*, 045504.
- (33) Pickard, C. J.; Needs, R. J. *Ab Initio* Random Structure Searching. *J. Phys.: Condens. Matter* **2011**, *23*, 053201.
- (34) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. First Principles Methods Using CASTEP. *Z. Kristallogr. - Cryst. Mater.* **2005**, *220*, 567–570.
- (35) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (36) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (37) Aydinol, M. K.; Kohan, A. F.; Ceder, G.; Cho, K.; Joannopoulos, J. *Ab Initio* Study of Lithium Intercalation in Metal Oxides and Metal Dichalcogenides. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *56*, 1354–1365.
- (38) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 1505–1509.
- (39) Aras, M.; Kiliç, C. Combined Hybrid Functional and DFT+U Calculations for Metal Chalcogenides. *J. Chem. Phys.* **2014**, *141*, 044106.
- (40) Nakamura, K.; Akiyama, T.; Ito, T.; Freeman, A. J. Half-Metallicity at Ferromagnetic/Antiferromagnetic Interfaces in Zinc-blende Transition-Metal Chalcogenides: A Full-Potential Linearized Augmented Plane-Wave Study within LDA+U. *J. Appl. Phys.* **2008**, *103*, 07C901.
- (41) Yu, L.; Lany, S.; Kykyneshi, R.; Jieratum, V.; Ravichandran, R.; Pelatt, B.; Altschul, E.; Platt, H. A. S.; Wager, J. F.; Keszler, D. A.; Zunger, A. Iron Chalcogenide Photovoltaic Absorbers. *Adv. Energy Mater.* **2011**, *1*, 748–753.
- (42) Badrudin, F. W.; Taib, M. F. M.; Hassan, O. H.; Yahya, M. Z. A. Effect of Lithium Intercalation on the Structural and Electronic Properties of Layered LiFeSO_4OH and Layered FeSO_4OH Using First-Principle Calculations. *Comput. Mater. Sci.* **2016**, *119*, 144–151.
- (43) Thompson, A.; Attwood, D.; Gullikson, E.; Howells, M.; Kim, K.-J.; Kirz, J.; Kortright, J.; Lindau, I.; Pianetta, P.; Robinson, A.; Scofield, J.; Underwood, J.; Vaughan, D.; Williams, G.; Winick, H. *X-ray Data Booklet*; Lawrence Berkeley National Laboratory: Berkeley, CA, 2009; pp 1–2.
- (44) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-ray Absorption Spectroscopy Using IFFEFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.
- (45) Borkiewicz, O. J.; Shyam, B.; Wiaderek, K. M.; Kurtz, C.; Chupas, P. J.; Chapman, K. W. The AMPIX Electrochemical Cell: a Versatile Apparatus for *In Situ* X-ray Scattering and Spectroscopic Measurements. *J. Appl. Crystallogr.* **2012**, *45*, 1261–1269.
- (46) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. Two-Dimensional Detector Software: From Real Detector to Idealised Image or Two-Theta Scan. *High Pressure Res.* **1996**, *14*, 235–248.
- (47) Qiu, X.; Thompson, J. W.; Billinge, S. J. L. PDFgetX2: a GUI-Driven Program to Obtain the Pair Distribution Function from X-ray Powder Diffraction Data. *J. Appl. Crystallogr.* **2004**, *37*, 678–678.
- (48) Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Bozin, E. S.; Bloch, J.; Proffen, T.; Billinge, S. J. L. PDFfit2 and PDFgui: Computer Programs for Studying Nanostructure in Crystals. *J. Phys.: Condens. Matter* **2007**, *19*, 335219.
- (49) Chapman, K. W.; Lapidus, S. H.; Chupas, P. J. Applications of Principal Component Analysis to Pair Distribution Function Data. *J. Appl. Crystallogr.* **2015**, *48*, 1619–1626.
- (50) Brostigen, G.; Kjekshus, A. Redetermined Crystal Structure of FeS_2 -Pyrite. *Acta Chem. Scand.* **1969**, *23*, 2186–2188.
- (51) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1*, 011002.
- (52) Barrett, C. S. X-ray Study of the Alkali Metals at Low Temperatures. *Acta Crystallogr.* **1956**, *9*, 671–677.
- (53) Loschen, C.; Carrasco, J.; Neyman, K. M.; Illas, F. First-Principles LDA+U and GGA+U Study of Cerium Oxides: Dependence on the Effective U Parameter. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 035115.
- (54) Boesenberg, U.; Marcus, M. A.; Shukla, A. K.; Yi, T.; McDermott, E.; Teh, P. F.; Srinivasan, M.; Moewes, A.; Cabana, J. Asymmetric Pathways in the Electrochemical Conversion Reaction of NiO as Battery Electrode with High Storage Capacity. *Sci. Rep.* **2014**, *4*, 7133.
- (55) Kostov, S.; denBoer, M.; Strauss, E.; Golodnitsky, D.; Greenbaum, S. G.; Peled, E. X-ray Absorption Fine Structure Studies of FeS_2 Cathodes in Lithium Polymer Electrolyte Batteries. *J. Power Sources* **1999**, *81*–82, 709–714.
- (56) Lytle, F. W.; Greegor, R. B. Discussion of X-Ray Absorption Near-Edge Structure: Application to Cu in the High- T_c Superconductors $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 1550–1563.
- (57) Szymański, J. The Crystal Structure of High-Temperature CuFe_2S_3 . *Z. Kristallogr. - Cryst. Mater.* **1974**, *140*, 240–248.
- (58) McDowell, M. T.; Lu, Z.; Koski, K. J.; Yu, J. H.; Zheng, G.; Cui, Y. In Situ Observation of Divergent Phase Transformations in Sulfide Nanocrystals. *Nano Lett.* **2015**, *15*, 1264–1271.
- (59) Page, K.; Proffen, T.; Terrones, H.; Terrones, M.; Lee, L.; Yang, Y.; Stemmer, S.; Seshadri, R.; Cheetham, A. K. Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction. *Chem. Phys. Lett.* **2004**, *393*, 385–388.
- (60) Tucker, M. G.; Keen, D. A.; Dove, M. T.; Goodwin, A. L.; Hui, Q. RMCProfile: Reverse Monte Carlo for Polycrystalline Materials. *J. Phys.: Condens. Matter* **2007**, *19*, 335218.

(61) Masset, P. J.; Guidotti, R. A. Thermal Activated (“Thermal”) Battery Technology Part IIIb: Sulfur and Oxide-based Cathode Materials. *J. Power Sources* **2008**, *178*, 456–466.