Supporting Information for:

Synthesis, Modular Composition, and Electrochemical Properties of Lamellar Iron Sulfides

Noah E. Horwitz, Elena V. Shevchenko, Jehee Park, Eungje Lee, Jiaze Xie, Baorui Chen, Yu Zhong, Alexander S. Filatov, John S. Anderson

Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United States
Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, United States
Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Correspondence to: jsanderson@uchicago.edu
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Additional Synthetic Procedures

1-Li, Method 3
Fe(DEDTC)₃ (25 mg, 0.05 mmol) and LiCF₃SO₃ (39 mg, 0.25 mmol) were added to a vial and dissolved in DMF (2.5 mL). In a separate vial, dithio-p-urazine (15 mg, 0.1 mmol) was dissolved in DMF (2.5 mL). The solutions were combined and heated in a sealed vial to 100 °C for 24 h. The resulting black solid was isolated via centrifugation, washed 2x with DMF (2 mL) and 3x with THF (2 mL) to obtain 1-Li (~7 mg, quant.).

1-Li, Method 4 (to prepare films for UV-visible-NIR spectroscopy)
Fe(EX)₃ (17 mg, 0.04 mmol) and LiCF₃SO₃ (31 mg, 0.2 mmol), and DMF (4 mL) were mixed and the resulting solution divided between two 4 mL vials. A sapphire substrate was added to each vial and the vials were maintained at room temperature for 2 days. During this time, a film of dark solid formed on the vial walls and the surfaces of the substrates. The substrates were washed 2x with DMF (2 mL) and 2x with THF (2 mL) before being dried under vacuum.

1-Na
Fe(DEDTC)₃ (25 mg, 0.05 mmol) and NaCF₃SO₃ (43 mg, 0.25 mmol) were added to a vial along with DMF (5 mL). The vial was sealed and shaken to dissolve all solids, then heated to 140 °C for 3 days. The resulting black solid was isolated via centrifugation, washed 2x with DMF (2 mL) and 3x with THF (2 mL) to obtain 1-Na.

1-K
Fe(DEDTC)₃ (25 mg, 0.05 mmol) and KCF₃SO₃ (47 mg, 0.05 mmol) were added to a vial along with DMF (5 mL). The vial was sealed and shaken to dissolve all solids, then heated to 140 °C for 3 days. The resulting black solid was isolated via centrifugation, washed 2x with DMF (2 mL) and 3x with THF (2 mL) to obtain 1-K.

1-TMA
Fe(DEDTC)₃ (25 mg, 0.05 mmol) and TMAPF₆ (55 mg, 0.05 mmol) were added to a vial along with DMF (5 mL). The vial was sealed and shaken to dissolve all solids, then heated to 140 °C for 3 days. The resulting black solid was isolated via centrifugation, washed 2x with DMF (2 mL) and 3x with THF (2 mL) to obtain 1-TMA.
Figure S1: $^1$H NMR spectrum of Fe(DEDTC)$_3$ in CDCl$_3$. 
Figure S2: $^1$H NMR spectrum of Fe(EX)$_3$ in CDCl$_3$. Small unlabeled peaks are due to traces of free ligand and methanol.
Figure S3. Representative SEM images of aggregates (a-b) and an isolated flake (d) of \textit{1-Li}. 
X-ray Powder Diffraction Measurements

**Figure S4:** XRPD patterns of materials synthesized from Fe(EX)₃ with different salt additives (all measured wet as suspensions in DMF).

**Figure S5:** XRPD patterns of 1-TMA wet with DMF and dried.
X-ray Fluorescence Data

Figure S6: Representative XRF spectrum of 1-Li.

X-ray Absorption (XAS) Data and Fits

Figure S7: Comparison of Fe K-edge XANES (first derivative) from 1-Li to literature data for mackinawite and greigite. Literature spectra adapted from Jeong et al., *Water Res.* 2013, 47, 6639-6649.
**Figure S8:** EXAFS data from 1-Li (wet in DMF) with fit to mackinawite model presented in k-space.

**Figure S9:** EXAFS data from 1-Li (wet in DMF) with a) R-space and b) k-space fits to smythite model.
Figure S10. EXAFS data from 1-Li (wet in DMF) with a) R-space and b) k-space fits to Li$_2$FeS$_2$ model.
Table S1: EXAFS fitting parameters for 1-Li (wet in DMF) using structural models from mackinawite, smythite, and Li$_2$FeS$_2$ crystal structures.

<table>
<thead>
<tr>
<th>Model</th>
<th>N</th>
<th>R (Å)</th>
<th>σ$_2$ (Å$^2$)</th>
<th>R-factor</th>
<th>Reduced chi-square</th>
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<tbody>
<tr>
<td>Mackinawite</td>
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<td>2.257(6)</td>
<td>0.0028(8)</td>
<td>0.0079</td>
<td>484</td>
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<tr>
<td>Fe$_1$-S</td>
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<td>2.71(2)</td>
<td>0.012(2)</td>
<td></td>
<td></td>
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<tr>
<td>Fe$_1$-Fe$_2$</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Independent points = 9.8, number of variables = 6, ΔE$_0$ = 1.3(7) eV, S$_0^2$ = 0.67(5), fitting range k = 2.1-12 Å$^{-1}$ and R = 1-2.6 Å, k weights = 1, 2, 3

<table>
<thead>
<tr>
<th>Model</th>
<th>N</th>
<th>R (Å)</th>
<th>σ$_2$ (Å$^2$)</th>
<th>R-factor</th>
<th>Reduced chi-square</th>
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<tr>
<td>Smythite</td>
<td></td>
<td>2.265(8)</td>
<td>0.004(1)</td>
<td>0.0097</td>
<td>802</td>
</tr>
<tr>
<td>Fe$_1$-S</td>
<td>6</td>
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<td>Fe$_1$-Fe$_2$</td>
<td>2</td>
<td>2.72(2)</td>
<td>0.003(2)</td>
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</table>

Independent points = 9.8, number of variables = 6, ΔE$_0$ = 1.6(8) eV, S$_0^2$ = 0.50(4), fitting range k = 2.1-12 Å$^{-1}$ and R = 1-2.6 Å, k weights = 1, 2, 3

<table>
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<th>Model</th>
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<th>R (Å)</th>
<th>σ$_2$ (Å$^2$)</th>
<th>R-factor</th>
<th>Reduced chi-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$FeS$_2$</td>
<td></td>
<td>2.26(1)</td>
<td>0.0040(9)</td>
<td>0.0022</td>
<td>286</td>
</tr>
<tr>
<td>Fe$_1$-S$_1$</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe$_1$-S$_2$</td>
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<td>2.67(6)</td>
<td>0.01(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_1$-Fe$_2$</td>
<td>3</td>
<td>2.73(1)</td>
<td>0.010(3)</td>
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Independent points = 9.8, number of variables = 8, ΔE$_0$ = 0(1) eV, S$_0^2$ = 1.03(9), fitting range k = 2.1-12 Å$^{-1}$ and R = 1-2.6 Å, k weights = 1, 2, 3

Figure S11: Comparison of EXAFS data from wet (DMF) and dry samples of 1-Li in a) R-space and b) k-space.
Thermogravimetric Analysis (TGA)

Figure S12: Thermogravimetric analysis data for three batches of 1-Li, measured under N₂ with a 5 °C/min ramp rate.
UV-visible-NIR Spectroscopy

Figure S13: UV-visible-NIR absorption data for 1-Li. a) UV-visible-NIR absorption spectrum of 1-Li on sapphire (0001) and sapphire blank. b) Comparison of Tauc plots assuming different types of transitions. The indirect allowed transition produces the most linear plot. c) Tauc plot for indirect allowed transition with linear fit corresponding to $E_g = 0.23$ eV. Dotted lines highlight the X-axis and the linear fit as a visual guide. d) Photograph of 1-Li on sapphire (0001) sample (center) in holder.
Variable-Temperature Electrical Conductivity

Figure S14: Relative electrical conductivity vs. temperature for a pressed pellet of 1-Li. The presence of two linear regions and a plateau near 100 K may indicate a phase transition at low temperatures.
Figure S15: Linear fit to high temperature region of the variable temperature electrical conductivity plot shown in Figure S14.
Mössbauer Spectroscopy

**Figure S16**: $^{57}$Fe Mössbauer spectrum of 1-Li collected at 80 K with fit to a two site model.

**Table S2**: Mössbauer fitting parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Site 1</th>
<th>Site 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer shift ($\delta$)</td>
<td>0.428(3) mm/s</td>
<td>0.446(4) mm/s</td>
</tr>
<tr>
<td>Quadrupole splitting ($\Delta E_Q$)</td>
<td>0.898(6) mm/s</td>
<td>2.79(6) mm/s</td>
</tr>
<tr>
<td>Relative area</td>
<td>0.42(1)</td>
<td>0.58(2)</td>
</tr>
<tr>
<td>Gaussian broadening, FWHM</td>
<td>0.90(2) mm/s</td>
<td>2.43(3) mm/s</td>
</tr>
</tbody>
</table>
IR Spectroscopy

Figure S17: FTIR spectrum of 1-Li prepared as a KBr pellet.

Electrochemical Measurements

Figure S18. Cyclic voltammograms (1 mV/s, 0.1 M LiCF$_3$SO$_3$ in DMF) of carbon paper electrode coated with 1-Li + 10% rubber slurry and control electrodes. Current densities are calculated using the geometric areas of the electrodes (2 cm$^2$).
Figure S19: Cyclic voltammetry data for 1-Li composite electrode in 0.1 M LiCF$_3$SO$_3$/DMF showing Faradaic features. Data is plotted as current/scan rate, which for a capacitor gives the capacitance in Farads. Pseudocapacitive features should show no scan rate dependence, while Faradaic features should decrease at higher scan rates.

Figure S20: Cyclic voltammograms of the same 1-Li composite electrode in different electrolytes, measured at 10 mV/s. LiOTf = LiCF$_3$SO$_3$. 
Figure S21: dQ/dV plot for 1-Li lithium ion cathode half cell tests at 0.1C.

Figure S22: Charge/discharge curves for 1-Li sodium ion cathode half cell tests. \( V = 0.005 - 3.0 \) V vs. Na, \( I = 30 \) mA/g, 1M NaPF\(_6\) in EC/DEC + 2w\% FEC.
Figure S23: dQ/dV plot for 1-Li sodium ion cathode half cell tests.

Figure S24: Cycling stability of 1-Li sodium ion cathode in half cell tests.