

Supporting Information

An alternate synthetic pathway to nanoscopic Li_2FeS_2 for energy storage

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Materials and Methods

Material Synthesis

Inside of an Ar-filled glovebox, 5.25 mmol benzophenone (Ph_2CO) [Sigma-Aldrich] was dissolved into 60 mL of diethylene glycol dimethyl ether (Sigma-Aldrich) on a hotplate set to 80°C. After full dissolution, 5.25 mmol lithium metal (MTI corp.) was added to the solution and was stirred for 4 h at 80°C producing a deep blue color (Fig. S1). Next, 2.5 mmol pyrite FeS_2 (Sigma-Aldrich) powder is added to the solution and stirred for 8 h at 80°C. The resulting Li_2FeS_2 powder was washed with excess diglyme and centrifuged three times within the glovebox and subsequently dried under vacuum. Subsequent heat treatment of the powder was also performed within the glovebox using a small box furnace at 800°C for 16 h in a graphite crucible. To synthesize Li_2FeS_2 via the solid-state method, 3 mmol of FeS (Sigma-Aldrich) and 3 mmol of Li_2S (Sigma-Aldrich) were ground together in a mortar + pestle then pressed into a pellet within an Ar-filled glovebox. The pellet was melted at 900°C and heated for 16 h in a graphite crucible and cooled naturally.

X-ray Diffraction (XRD)

Samples for X-ray diffraction were prepared within an Ar-filled glovebox. Powders were pressed into a zero-background Si plate well and covered with Kapton tape to prevent exposure to air. Mounted samples were then tested using a Rigaku MiniFlex diffractometer and $\text{Cu K}\alpha$ radiation (1.5406 Å).

Scanning Electron Microscopy (SEM)

Powdered samples were adhered to Cu tape and mounted on Al stubs within an argon filled glovebox. The mounted samples were sealed within glass vials and transferred into a JEOL JSM-7600F and evacuated immediately to reduce air exposure. Images were taken at 15 kV with a working distance of 6 – 8 mm.

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

Inside an argon filled glovebox, 1.0 mg of chemically lithiated Li_2FeS_2 and 1.3 mg of solid-state synthesized Li_2FeS_2 were weighed into separate vials. Outside the glovebox, the samples were charged with 1 mL 5 % nitric acid in water and then heated at 70 °C for 5 min. After cooling, all

solids were visibly dissolved. The cooled solutions were then each diluted to 100 mL volume using 5 % nitric acid, yielding the samples for analysis. The ICP-OES was performed on an Agilent 5900 ICP-OES. All samples and standards were prepared in 5% nitric acid. Six standards were prepared ranging from 0.01 mg/L to 10 mg/L Li and Fe concentration in addition to a blank. Additional operating parameters are listed in Table 1.

Table 1. Operating Conditions for ICP-OES.

Gas	UHP argon
Replicate count	3
Pump speed (rpm)	12
Rinse time (s)	30
Read time (s)	5
RF power (KW)	1.2
Viewing mode	Radial
Viewing height (mm)	8
Nebulizer flow (L/min)	0.7
Plasma flow (L/min)	12
Aux flow (L/min)	1

Electrochemical Characterization

Electrodes were prepared by manually grinding a 60:20:20 (wt:wt:wt) mixture of Li_2FeS_2 :Super P carbon:PTFE powder and pressing the mixture into a $\frac{1}{2}$ " diameter Ni foam disc inside of an Ar-filled glovebox. The average active material loading was 0.8 mg cm^{-2} . For electrochemical evaluation, the Li_2FeS_2 @Ni foam electrode was placed within a type 2032 stainless-steel coin cell (MTI corp.) with a Whatman glass fiber separator, 150 μL of 1.0 M lithium hexafluorophosphate in EC:DEC electrolyte (Aldrich), and a Li metal counter electrode (Li chip, MTI corp.).

Using a Gamry Reference 620 potentiostat, the resulting coin cell containing the Li_2FeS_2 electrode was interrogated via cyclic voltammetry between 3.0 and 1.7 V at a scan rate of 0.1 mV/s. Galvanostatic charge/discharge measurements were conducted at a rate of 0.1 C with respect to nominal $1e^-$ theoretical capacity of $200 \text{ mAh g}^{-1} \text{ Li}_2\text{FeS}_2$.



Fig. S1 Photograph of the blue $\text{Ph}_2\text{Co}:\text{Li}$ 1:1 adduct in diglyme solvent.

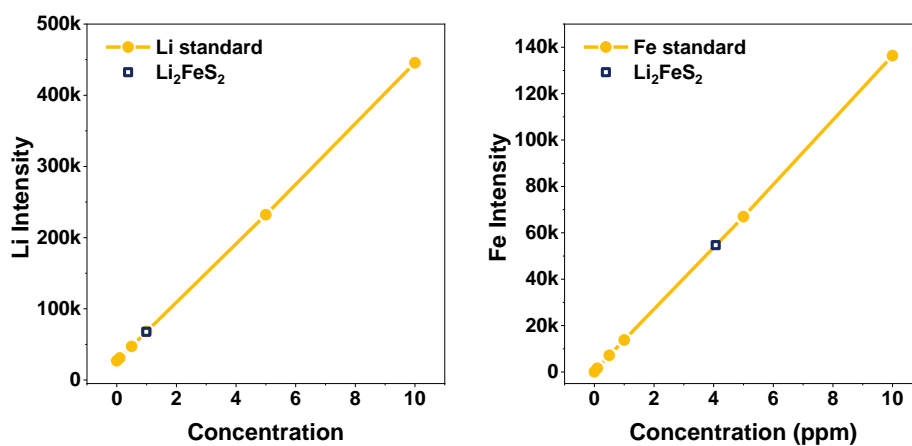


Fig. S2 Inductively coupled plasma optical emission spectrometry (ICP-OES) results for $\text{CL-Li}_2\text{FeS}_2$. The assumed final composition of the material is $\text{Li}_{1.95}\text{FeS}_{2.18}$ by assuming that all sulphur is lost to H_2S generation during air exposure and dissolution in nitric acid.

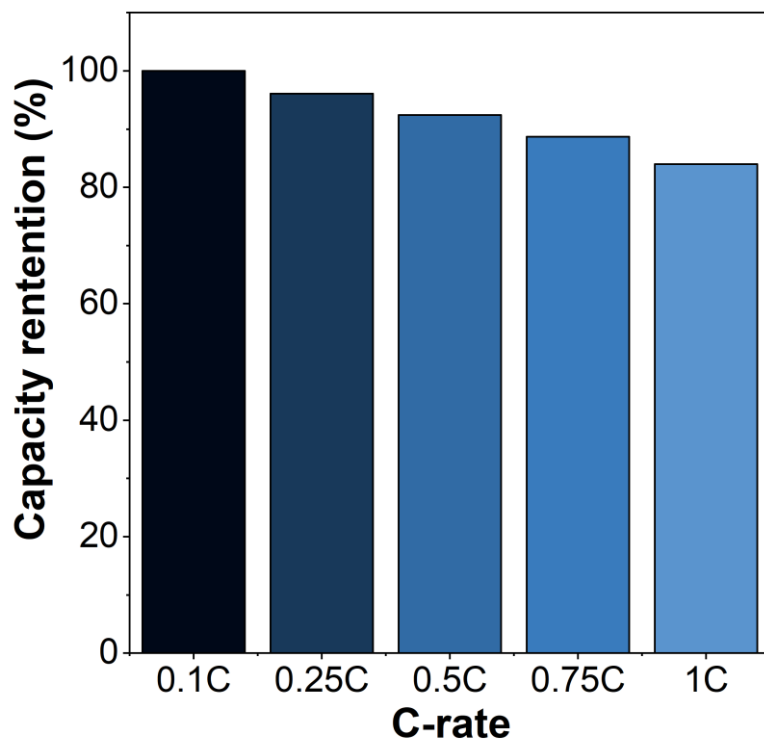


Fig. S3 Discharge capacity retention of $\text{Li}_2\text{FeS}_2:c./800$ for increasing C-rate (based on $1 e^-$ redox; 200 mAh g^{-1}).

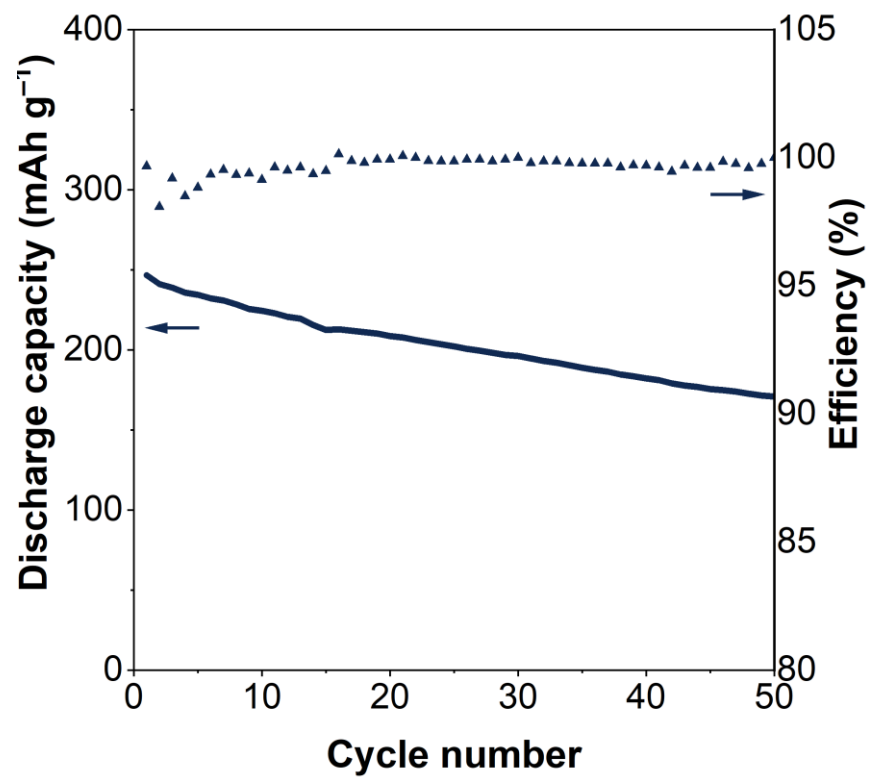


Fig. S4 Cycling retention of $\text{Li}_2\text{FeS}_2:c./l.800$ at 0.25C (based on $1 e^-$ redox; 200 mAh g^{-1}).

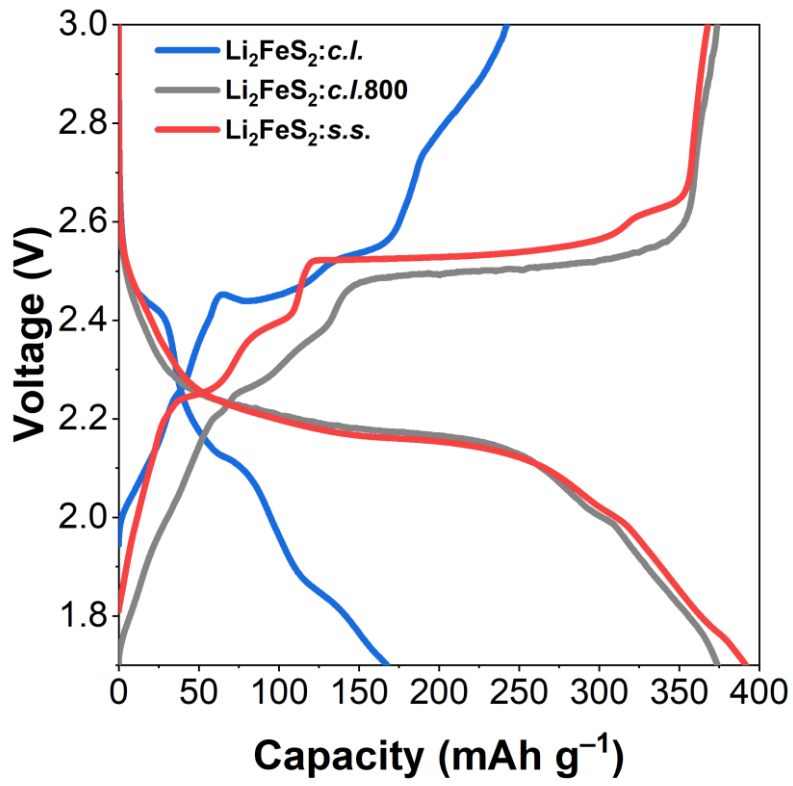


Fig. S5 Comparison of galvanostatic charge/discharge (20 mA g⁻¹) for Li₂FeS₂:c.l., Li₂FeS₂:c.l.800, and Li₂FeS₂:s.s. in a half-cell configuration.