

Analytical Exploration of Iron Disulfide Performance in Molten Salt Batteries

Noah B. Schorr*, *Teal Harbour, Martin B. Nemer, Hans W. Papenguth, Samantha Reyes, and John H. Taphouse*

Sandia National Laboratories
Albuquerque, NM, USA
nschorr@sandia.gov

Abstract

Molten salt batteries play a vital role as a long shelf-life power source in a variety of single use defense applications. In this work we focus on the performance of iron disulfide as an active cathode material for molten salt batteries that operate at ~500°C and identifying the properties of the material that influence performance. Various iron disulfide powders are investigated, with particles ranging from ~5 – 100 μm in size. A suite of analytical techniques has been used to determine physical and chemical properties of the iron disulfide particles. Using this information, we contrast the discharge performance of single cell molten salt tests. To better correlate properties from the electrochemical data with other analytical data, all cells tested are cathode capacity limited, eliminating anode contributions to recorded voltage transitions. Three discharge profiles are also applied to each iron disulfide investigated to probe multiple aspects of the relationship between physical properties and electrochemical performance. This work advances our understanding of iron disulfide as a cathode material for molten salt batteries and ultimately will assist in the selection of material based on desired performance.

Keywords

Iron disulfide; molten salt battery; single cell; electrochemistry; particle size; morphology.

Introduction

Batteries that use a molten salt electrolyte are ideal for single use devices that require minimal discharge during storage and access to high current densities when activated. In this work we explore iron disulfide as the cathode material in molten salt batteries (MSB). Specifically, six FeS₂ materials are analyzed using a suite of analytical techniques and electrochemical evaluations. In single cells the FeS₂ was discharged versus a lithium-silicon alloy anode with a LiCl-KCl mixture serving as the electrolyte. While pyrite is a known material for MSBs, often only a single source of the dichalcogenide is examined under different conditions or a single commercial-off-the-shelf product is compared to a synthetic material. By conducting experiments with a variety of FeS₂ powders we ascertain which physical and chemical properties are most important to the MSB discharge performance.

Experimental

Pyrite was procured from five different sources, with two powders acquired from a single vendor. All powders were processed in a moisture free dry room. For single cell experiments the pyrite powders were combined in a 75:25 wt% ratio with a premixed electrolyte-binder of MgO and LiCl-KCl. The FeS₂ was not processed in any fashion before mixing. The FeS₂ powder mixture was then pressed into 1" diameter cathode pellets. An oversized MgO based pellet with eutectic electrolyte was used as the separator and the cell was completed with an oversized Li₁₃Si₄ anode (both 1.25" diameter). The FeS₂ pellets had a theoretical capacity of 1418 As (394 mAh), for the full conversion of FeS₂ to Fe and Li₂S and the anode 1723 As (478 mAh) for the Li₁₃Si₄ to Li₇Si₃ transition.

All electrochemical tests were performed in an Ar filled glovebox with O₂ and H₂O < 1 ppm. Assembled single cells were placed between platens heated to 500 °C. Three different profiles done in triplicate, unless otherwise noted, were performed on each of the six FeS₂ materials. The first test was a discharge at a 1 C rate, where C rates are defined by the first transition capacity of the FeS₂ (1206 As/g). Second, cells were held at 500°C for 1 hr before discharging at 1 C. Third, a constant areal current density of 50 mA/cm² was applied along with series of four pulses lasting for 5 s with a 10 s return to 50 mA/cm² between pulses. Each pulse series included four pulses of increasing magnitude (125, 250, 500, 625 mA/cm²; 0.6334, 1.2668, 2.5334, 3.1669 A).

Results and Discussion

To focus on the FeS₂ properties the MSB single cells were designed to be cathode limited in capacity. This was done to ensure the alloy transition of the anode would not cause a change in cell voltage during the discharge. Borrowing a technique that is commonplace in Li-ion battery research, we undersized the FeS₂ pellet compared to the separator and anode. To ensure this geometry manipulation would produce reliable and reproducible results a 1.25" diameter cathode of the same composition was tested. As seen in Figure 1 the 1" FeS₂ pellet outperformed the 1.25" pellet in capacity utilization and in discharge voltage. Due to the favorable performance of the 1" diameter cathode when compared in

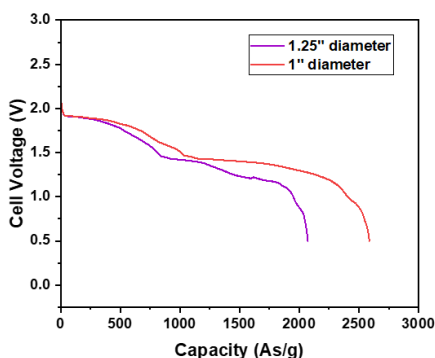


Figure 1. Constant current 1 C discharge comparison of two different sized FeS₂ pellets. Cathodes were fabricated using the same source of FeS₂.

triplicate for each size (not shown) we moved forward with this size pellet for all subsequent electrochemical tests.

The six different FeS₂ powders investigated all performed differently when discharged at a constant current (Figure 2A). When discriminating performance of the cells, four voltage regimes were chosen to quantify capacity; > 1.92 V (transient voltage and capacity), 1.8 – 1.5 V (high voltage), 1.5 – 0.5 V (first transition FeS₂ → Li₃Fe₂S₄), 0.5 V (voltage cutoff, total capacity). These regions are marked in Figure 2B. In Table 1 the capacities of the various regions of the discharge are given for each sample.

The same constant current discharge profile was then used on the six different materials but with a 1 hr open circuit voltage (OCV) hold before sourcing a current. The capacity values from this discharge profile are recorded in Table 2. Except in sample 2, every capacity has decreased after the heating during the 1 hr OCV. This is unsurprising given the known phenomenon of self-discharge in FeS₂ based MSBs.¹ The largest percent change of capacity loss due to heating was in the transient regime. Represented in Figure 3A, in cells heated for 1 hr essentially no transient capacity was produced. This tracked with a similar trend of a decrease in

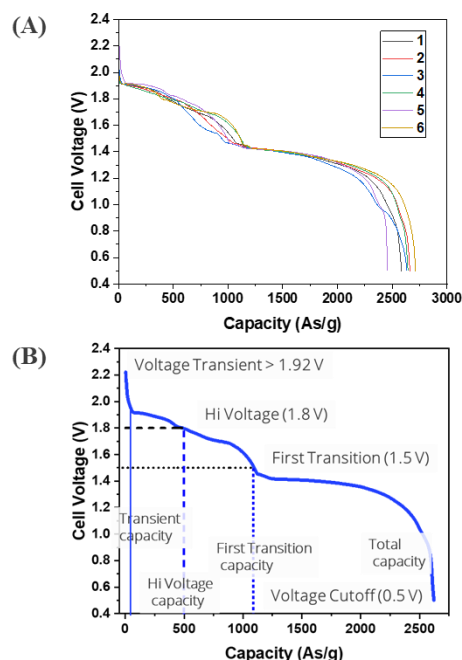


Figure 2. (A) Constant current 1 C discharge comparison six different FeS₂ cathodes. **(B)** Voltage cutoffs and the associated capacity regimes used to analyze the MSB discharge curves.

maximum voltage produced by the cell under load. A decrease in maximum voltage and loss of transient capacity indicates impurities or iron phases reacted at an elevated temperature. It should be noted that only sample 5, with the highest voltage and transient capacity, showed any contaminants (Zn, As, Cu, Al) above 1000 ppm when analyzed by elemental analysis. The consistent maximum voltage from each sample after the preheat indicates a stabilization of the FeS₂ polarization with a lower potential phase.

Ideally an FeS₂ cathode would not lose any capacity upon reaching the operating temperature of the MSB, but most

Table 1. Utilized capacity (As/g) of cells at different voltage regimes from a constant current 1 C discharge.

Sample	Transient Capacity (>1.92 V)	+/-	Hi Voltage (1.8 V)	+/-	First Transition (1.5 V)	+/-	Total Capacity (0.5 V)	+/-
1	23.8	2.2	480	30	1062	15	2560	53
2	16.74	0.44	474	24	994	68	2514	140
3	34.9	4.4	523	49	995	45	2560	89
4	9.9	2.8	455	25	1159	39	2684	42
5	69.6	1.7	577	6	1019	22	2512	52
6	24.03	0.52	425	25	1122	10	2699	11

Table 2. Utilized capacity (As/g) of cells that underwent 1 hr at 500°C before discharging at a 1 C rate.

Sample	Transient Capacity (>1.92 V)	+/-	Hi Voltage (1.8 V)	+/-	First Transition (1.5 V)	+/-	Total Capacity (0.5 V)	+/-
1	0.16895	0.00043	371	42	874	29	2510	14
2	0.1599	0.0079	481	25	953	53	2602	39
3	0.16886	0.00012	389	30	812	37	2393	58
4	0.085	0.029	352	16	851	7	2319	118
5	0.95	0.39	354	5	750	18	2378	35
6	0.173	0.020	332	56	935	12	2610	30

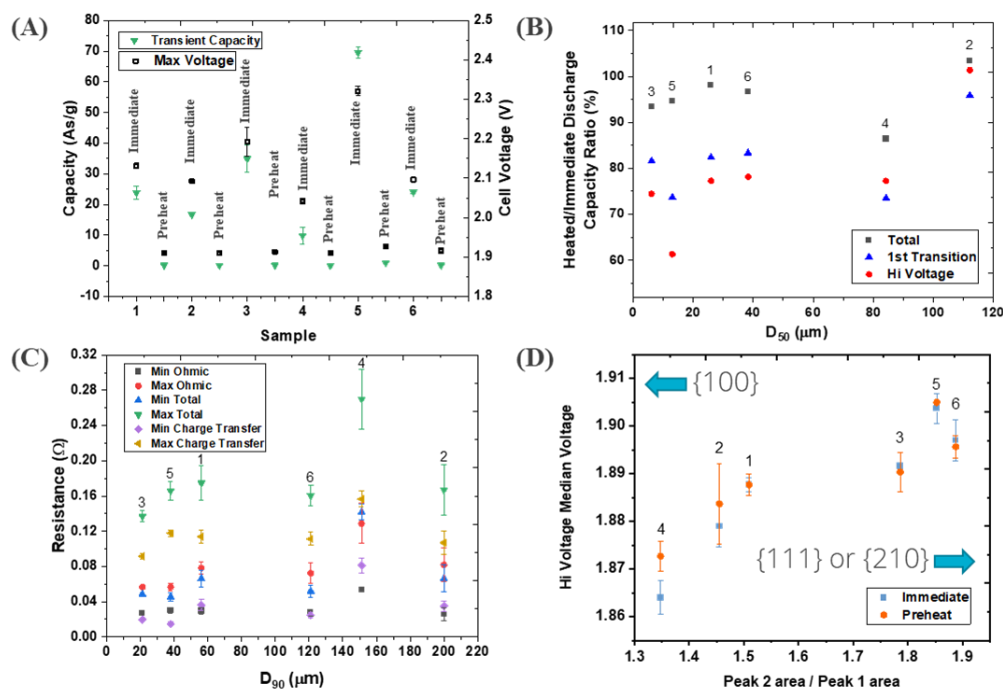


Figure 3. (A) Plot of the transient capacity above 1.92 V and the maximum cell voltage during an applied load. Each sample has four associated points, the two above the sample number are from the immediate constant current discharge and the points to the right are from the preheat discharges. (B) Scatter of the capacity ratio of the preheat discharge to immediate discharge compared against the average FeS₂ particle size in microns. (C). Resistance values of samples plotted versus the D₉₀ particle size in microns. (D) Plot of the high voltage median voltage versus the peak area ratio (A_g/E_g).

electrodes suffer from active material loss. Figure 3B shows the capacity ratio of the heated and immediately discharged cells vs average particle size, where a larger percentage indicates less capacity loss from the 1 hr OCV hold at 500°C. capacity. However, sample 2 retained above 95% of these capacities. This led sample 2 to have the best high voltage capacity after preheating, even though it ranked fourth in this category when immediately discharged. Most materials preform similarly, losing 75-85% of the high voltage and first transition.

When comparing the capacity retention ratio, as seen in Figure 3B, a clear trend did not emerge with particle size. Sample 2, which had the best retention, has the largest average particle size but sample 4, which has the second largest average particle size did not have a better retention than smaller FeS₂ samples 3, 1, or 6. Powders with larger particles having better retention would be expected due to the increase in temperature of degradation observed in thermogravimetric analysis (not shown).

In pristine cells the six FeS₂ samples were discharged using a pulse protocol to acquire information about the cell resistance. The minimum and maximum calculated resistance values for the six samples is shown in Figure 3C. By comparing against the D₉₀ particle size none of the resistance values follow a particular trend. Samples 6 and 2 show similar resistance values to powders containing largest particles which are less than half the size. Sample 4 had the highest resistance of any sample, indicating that there is not

a direct correlation between the largest particle size and resistance or there are unique properties of samples 2 and 6.

Raman spectroscopy is a valuable tool to look at polarizable bonds in materials. Pyrite is known to have active vibrational modes including the sulfur bend (E_g) and sulfur stretch (A_g).² demonstrated that the ratio of these two peaks correlated with the predominant exposed Miller index faces of particles in the FeS₂ powder. Reference 3 showed that crystals irradiated by a normal incident laser a peak ratio closer to 1 indicated an exposed {100} faces and values of 1.8 and 2.1 were collected for {111} and {210}. When this ratio was calculated for the six samples the strongest trend emerged when compared to the high voltage median voltage (Figure 3D). The samples with lower average voltage values have lower ratios. This includes sample 4 with the lowest peak ratio, indicating an exposed {100} faces, and lowest median high voltage. The exposed crystal orientation only impacting the high voltage regime makes intuitive sense since as the exposed FeS₂ reacts first leaving the remaining particle to discharge without a preferred directionality.

The lack of correlation between electrochemical and particle size, thermal, and structural analysis is an unexpected result. The general absence of trends in the data presented above, when examined exclusively, implies another factor or certain combination of factors is controlling the FeS₂ discharge behavior. Images of the six samples were taken with a scanning electron microscope (SEM) to identify particle morphology (Figure 4). While samples 1, 3, 4, and

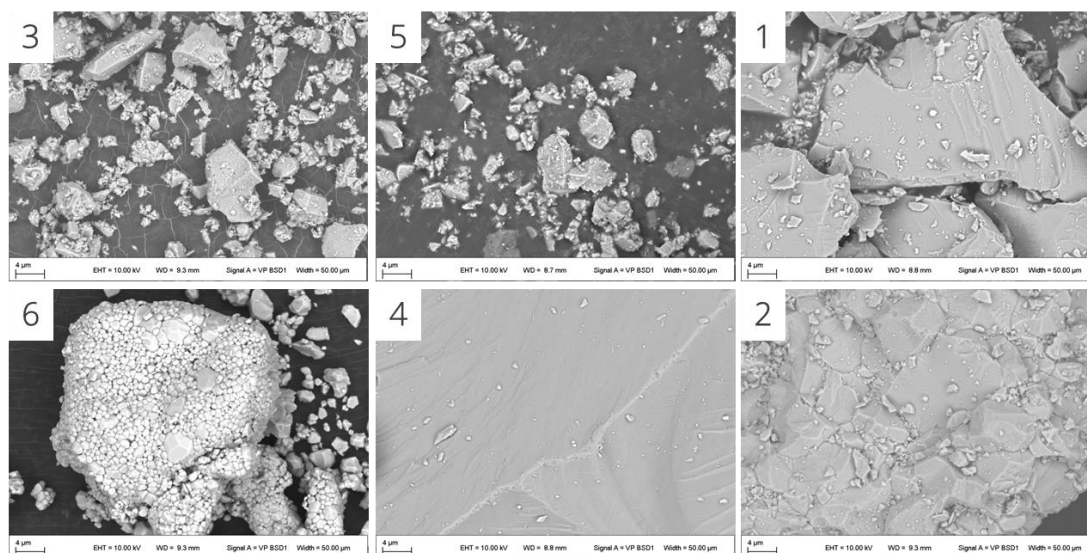


Figure 4. SEM images of the six FeS₂ powders shown in increasing average particle size (left to right). All images were taken under the same magnification, scale bar is 4 μm.

5 share the similar appearance of a broken-up crystal, samples 2 and 6 display different surface morphologies. Sample 6 appears to have the highest surface area and the particles are agglomerates of smaller FeS₂ structures. Sample 2 has a rougher surface than samples 1, 3, 4, and 5. The greater surface area of samples 6 and 2 is likely the reason why these samples have resistance values closer to the smaller particles. The larger particle size and high surface area characteristics could also play an essential role in sample 2 and 6, which have the largest high voltage and first transition capacities retentions after heating at 500°C for 1hr. SEM characterization of particles enables discrimination between vendors' products not achievable through more quantitative methods.

Conclusion

Six different FeS₂ powders were investigated for use as the active material in molten salt battery cathodes. Single cells were discharged using three current profiles to evaluate the electrochemical performance of the various pyrites. The voltage, capacity, and resistance taken from these tests were compared to chemical and physical analyses of the powders. Some trends emerged, but no single chemical or physical feature of the FeS₂ powders could fully explain the cell discharge performance. However, when using particle size and surface structure metrics, the voltage and capacity retention are rationalized.

Acknowledgements

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any

subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

This article has been authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The employee owns all right, title and interest in and to the article and is solely responsible for its contents. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this article or allow others to do so, for United States Government purposes. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan <https://www.energy.gov/downloads/doe-public-access-plan>.

The authors wish to thank Linda Johnson, Alan Harrington, Bertha Montoya, and Martin Salazar for technical input.

References

1. Masset, P.J., Guidotti, R.A., "Thermal activated ("thermal") battery technology Part IIIa: FeS₂ cathode material" *J Power Sources*, vol. 177, pp. 595-609, 2008.
2. Vogt, H., Chattopadhyay, T., Stoltz, H.J., "Complete First-order Raman Spectra of the Pyrite Structure Compounds FeS₂, MnS₂, and SiP₂," *J. Phys. Chem Solids*, vol. 44, no. 9, pp 869-873, 1983.
3. Bryant, R.N., Pasteris, J.D., Fike, D.A., "Variability in the Raman Spectrum of Unpolished Growth and Fracture Surfaces of Pyrite Due to Laser Heating and Crystal Orientation," *Applied Spectroscopy*, vol. 72(1), pp. 37-47, 201