

Solid-State Batteries

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Influence of Iron Sulfide Nanoparticle Sizes in Solid-State Batteries**

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Abstract: Given the inherent performance limitations of intercalation-based lithium-ion batteries, solid-state conversion batteries are promising systems for future energy storage. A high specific capacity and natural abundancy make iron disulfide (FeS_2) a promising cathode-active material. In this work, FeS_2 nanoparticles were prepared solvothermally. By adjusting the synthesis conditions, samples with average particle diameters between 10 nm and 35 nm were synthesized. The electrochemical performance was evaluated in solid-state cells with a Li-argyrodite solid electrolyte. While the reduction of FeS_2 was found to be irreversible in the initial discharge, a stable cycling of the reduced species was observed subsequently. A positive effect of smaller particle dimensions on FeS_2 utilization was identified, which can be attributed to a higher interfacial contact area and shortened diffusion pathways inside the FeS_2 particles. These results highlight the general importance of morphological design to exploit the promising theoretical capacity of conversion electrodes in solid-state batteries.

Iron disulfide FeS_2 has been explored as a high-energy, abundant and environmentally friendly material for electrochemical energy storage.^[1–3] While Li- FeS_2 primary batteries are commercially available, the poor reversibility has limited the application of rechargeable cells. Compared to intercalation-type active materials, conversion reactions of transition

metal sulfides often suffer from limited reversibility due to sluggish kinetics, detrimental volume changes and the often insulating character of reaction products.^[4–6] With the goal of enabling the reversible four-electron energy storage in FeS_2 -based cathodes nanostructuring of active materials seems promising.^[7,8] In Li- FeS_2 cells, the influence of the FeS_2 crystallite size on the cell performance has been studied in the past with both liquid and solid electrolytes as slow lithium diffusion within FeS_2 results in kinetic limitations.^[9–11] By improving the reaction kinetics and lowering the needed Li^+ diffusion pathways with reduced particle sizes, the reversibility and rate capability has been improved.^[12,13]

Nevertheless, similar to Li-S batteries, the detrimental dissolution of polysulfides is possible in Li- FeS_2 batteries,^[14,15] and a potential mitigation strategy could be the use in solid-state batteries.^[16] Whereas sulfide-based solid electrolytes suffer from oxidative decomposition in contact to high-voltage intercalation electrodes, the lower redox potential of FeS_2 possibly better agrees with the oxidative stability limit of thiophosphates.^[17–19] This constitutes an additional advantage for using FeS_2 as a cathode active material.

Thus, inspired by the promising option of tailoring the particle sizes of FeS_2 and their potential use in solid-state batteries, in this work we prepared FeS_2 nanoparticles with various size distributions and characterized their electrochemical performance in solid-state batteries. Reduced FeS_2 nanoparticle sizes showed a positive impact on the total capacity and rate capability, highlighting the potential of nanosized FeS_2 as cathode active conversion material in solid-state batteries.

The FeS_2 nanoparticles were prepared solvothermally and all experimental details can be found in the Supporting Information. Figure 1a shows the X-ray diffraction patterns of the as-obtained FeS_2 samples in which all intensities can be assigned to cubic FeS_2 without detectable crystalline impurities. By varying the ratio of oleic acid (OAc) to oleylamin (OAm), denoted as OAc:OAm, different particle size distributions were obtained. The different average particle sizes are evaluated using a Pawley fit (see Supporting Information),^[20] and three different average particle sizes of $11(\pm 0.3)$ nm, $33(\pm 0.3)$ nm and $36(\pm 0.5)$ nm are found. Transmission electron microscopy (TEM) was used to evaluate the particle size distribution (Figure 1b,c). For reasonable statistics, around 100 particles of a representative sample section were analyzed. Particle diameters were calculated by assuming an ideal spherical particle shape based on the measured area. For the FeS_2 samples in this study, a decreased OAc:OAm ratio was found to result in reduced particles sized. Consequently, the smallest particles in the range of 5–15 nm were found for an OAc:OAm ratio of 1:2. Overall, average particle sizes of $9.7(\pm 1.3)$ nm, $22.1(\pm 1.5)$ nm and

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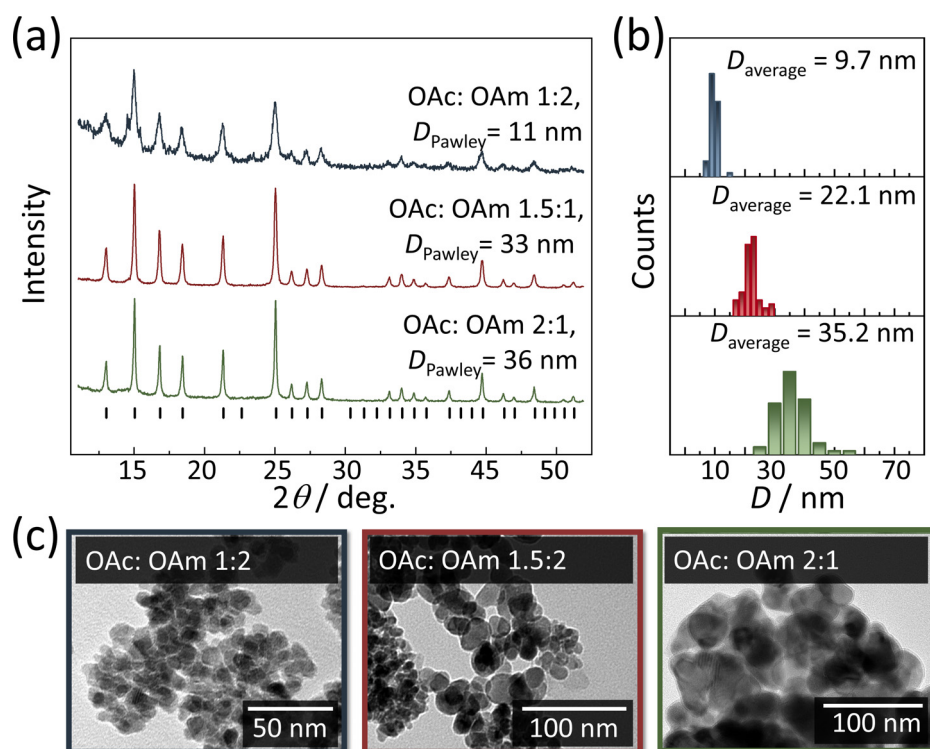


Figure 1. (a) X-ray diffractograms of FeS₂ nanoparticles from solvothermal reactions as a function of oleic acid (OAc): oleylamine (OAm) ratios: 1:2 (blue), 1.5:1 (red) and 2:1 (green), recorded with Mo K α radiation. Average particle sizes are estimated and shown as insets based on Pawley fitting. (b) Particle size distributions of as-synthesized FeS₂ particles from TEM imaging. (c) TEM images of the as-synthesized FeS₂ particles. For an OAc:OAm ratio of 1:2, particle sizes were in the range of 5–15 nm, OAc:OAm ratios of 1.5:1 and 2:1 resulted in larger particles.

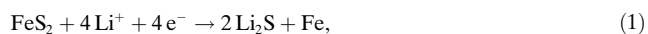
35.2($\pm$ 4.9) nm are found via TEM, which corroborate the sizes obtained from X-ray diffraction.

Solid-state In/InLi | Li₆PS₅Cl | FeS₂-Li₆PS₅Cl-C cells were assembled to evaluate the influence of the FeS₂ nanoparticle sizes on the resulting electrochemical properties. Cathodes were prepared with a FeS₂ loading of 3.8 mg cm⁻². In order to ensure sufficient ionic and electronic charge transport within

the cathodes, high volume fractions of carbon and solid electrolyte (23 vol% C, 63 vol% Li₆PS₅Cl) were employed.^[21] Unlike conventional layered oxide cathode materials, FeS₂ is discharged in the initial cyclization step. The subsequent charge-discharge cycle is defined as first cycle in the following.

Figure 2 shows the potential profile for the initial discharge and the following charge-discharge cycles of an exemplary cell. The initial discharge differs from the subsequent steps. During the initial discharge, two slopes indicate that different reduction reactions are occurring. Accordingly, two slopes are observed in the following first charge. Importantly, the high initial discharge capacity of 760 mAh g⁻¹ cannot be recovered during charging. Comparing initial and first discharge, the latter is characterized by significantly higher potentials and a lower overall capacity. Based on this complex behavior, the underlying cell reactions are likely highly convoluted. The

overall four-electron reduction of FeS₂ during the initial discharge is typically described by [Eq. (1)]



corresponding to a theoretical specific capacity of 894 mAh g⁻¹. As the initial discharge capacity is close to this value, contributions of both Fe^{+III} and S^{-I} reduction are expected here. Commonly, a two-step reaction via reduction of FeS₂ to Li₂FeS₂ followed by reduction to Fe⁰ and Li₂S, is assumed.^[22,23] During charging, the formation of multiple electrochemically active species, for instance S, FeS_x and Li_xFeS₂, was reported before and may be at play here, especially since the significant difference between initial and first discharge is observed.^[24,25] Yersak et al. attributed the irreversibility of the initial discharge to the formation of orthorhombic FeS₂ during the first charge,^[9] but formation of Fe⁰ can also be expected to lead to irreversibility. Additionally, volume changes of the active material during cycling need to be considered together with chemomechanical degradation.^[26] Furthermore, reductive decomposition of the electrolyte Li₆PS₅Cl may be expected during the initial discharge,^[18,27] and a certain additional capacity from the solid electrolyte seems possible.^[19] However, the decomposition of the solid electrolyte seems negligible, considering the minor changes in the X-ray photoemission spectra (see below). Consequently, the irreversible capacity of the initial discharge

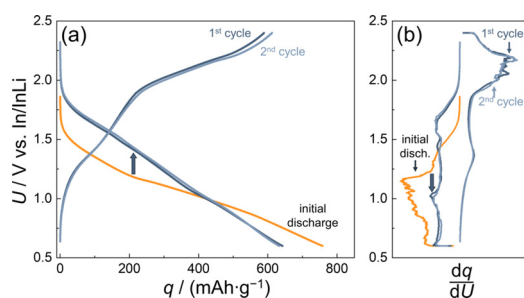


Figure 2. Typical potential profiles of initial discharge (orange) and the subsequent cycles (blue) of InLi/Li₆PS₅Cl/FeS₂-C-Li₆PS₅Cl cell with an average FeS₂ particle size $\bar{D}$ of 9.7 nm. The initial discharge is characterized by two slopes and a high capacity of 760 mAh g⁻¹. Two processes are observed for the following charging. However, the subsequent discharge steps differ significantly from the initial reduction of FeS₂. Besides cycling of FeS₂ and associated phases, reductive/oxidative decomposition of Li₆PS₅Cl and cycling of decomposed phases are expected in this potential range.

is most likely caused by a superposition of the partial irreversible reduction of FeS_2 , electrochemical electrolyte degradation and chemomechanical losses. Overall, a resulting complex mixture of multiple redox-active species during the initial discharge and the following charge seems to occur in FeS_2 based solid state batteries.

By comparing the electrochemical performance of FeS_2 - $\text{Li}_6\text{PS}_5\text{Cl}$ cathodes, the influence of FeS_2 particle size on the electrochemical utilization is highlighted (Figure 3). While the potential profiles show similar characteristics for all investigated samples, the overall capacity as well as the performance at higher cycling rates is improved by reduced particle sizes, despite the slightly higher overall cell resistances (see Supporting Information S5). Within the investigated period of 40 cycles, continuous capacity fading is observed, which is stressed for the sample with the smallest particles. This trend can possibly be explained by the higher interfacial area between FeS_2 and conducting cathode matrix for smaller particles.

In order to elucidate the underlying processes and differences of different particle sizes during cyclization in FeS_2 -C- $\text{Li}_6\text{PS}_5\text{Cl}$ cathode composites, the composites were character-

ized *post-mortem* by X-ray photoelectron spectroscopy (XPS). All the S 2p and P 2p spectra for the $\text{Li}_6\text{PS}_5\text{Cl}$ can be found in the Supporting Information. Most likely due to a low overall atomic fraction of Fe in the investigated cathode composites (approx. 5 at.-%), the Fe spectra cannot be resolved. Figure 4 shows S 2p detail spectra of the pristine FeS_2 particles as well as the cathode composites at different charged and discharged states during cyclization. Besides the expected S_2^{2-} main contribution at around 162.5 eV, both reduced and oxidized sulfur species appear. A broad peak ($E(2p_{3/2}) = 163.6$ eV) can be correlated to the presence of sulfur and long-chain sulfides. Additionally, peaks at higher binding energies (167–169 eV) are found for all samples, which can be assigned to sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) species.^[28,29] A reduced species ($E(2p_{3/2}) = 161.4$ eV) can be attributed to sulfide ions (S^{2-}), possibly due to FeS as side product.^[22,30] These contributions cannot be fully deconvoluted due to peak overlap. Sulfate and sulfite species have been identified by XPS analyses on solvothermally synthesized FeS_2 before and were attributed to surface species.^[31] Therefore, these additional phases may just be part of the spectra due to the high surface sensitivity of XPS and the high surface to bulk ratio of the FeS_2 nanoparticles. After adding the solid electrolyte $\text{Li}_6\text{PS}_5\text{Cl}$, the contributions of FeS_2 and the solid electrolyte in the resulting cathode composite are strongly convoluted. The S 2p detail spectrum of pristine $\text{Li}_6\text{PS}_5\text{Cl}$ shows a main contribution at 161.6 eV of the PS_4^{3-} tetrahedra as well as the free S^{2-} anion at 160.0 eV. While small differences in binding energies impede the resolution of the individual sulfur contributions (S_2^{2-} in FeS_2 , S^{2-} and PS_4^{3-} in $\text{Li}_6\text{PS}_5\text{Cl}$), significant changes in S 2p spectra indicate different sulfur oxidation states in the discharged and charged samples. A clear increase in intensity of the reduced sulfur species S^{2-} can be found after the initial cell discharge. During the subsequent charge, (partial) re-oxidation shows the contribution of sulfur to the cell capacity as the S^{2-} signal decreases again. In comparison between cathodes with varied FeS_2 particle sizes, less severe changes upon cyclization are observed in the S 2p spectra for larger FeS_2 particle sizes (Figure 4b). The lower intensity of the reduction to S^{2-} for the larger average particle sizes is in accordance with the lower capacity observed during cycling and can be interpreted as hindered active material utilization for larger FeS_2 particle sizes.

While the exact deconvolution of contributions here is difficult, due to the superposition of FeS_2 , $\text{Li}_6\text{PS}_5\text{Cl}$ and possible other decomposition products, certain information can be inferred. During the initial discharge, the $(\text{S}_2)^{2-}$ in FeS_2 will mostly be reduced to Fe^0 and S^{2-} , forming Li_2S , while reduction of P^{5+} would result in the decomposition of crystalline $\text{Li}_6\text{PS}_5\text{Cl}$ as recently observed.^[18,27] In the following charge, oxidation of Li_2S as well as possible Fe must be expected to result in the observed multiple redox-active phases. In Li- FeS_2 cells, Fong and Dahn suggested that FeS_2 , FeS , and S are formed during charging.^[24] For the oxidative conditions, decomposition of $\text{Li}_6\text{PS}_5\text{Cl}$ to S, P_2S_5 and LiCl was predicted theoretically.^[32] However, considering the P 2p spectra of the cycled FeS_2 - $\text{Li}_6\text{PS}_5\text{Cl}$ -C cathodes, minor changes are found that suggest that the dominant electro-

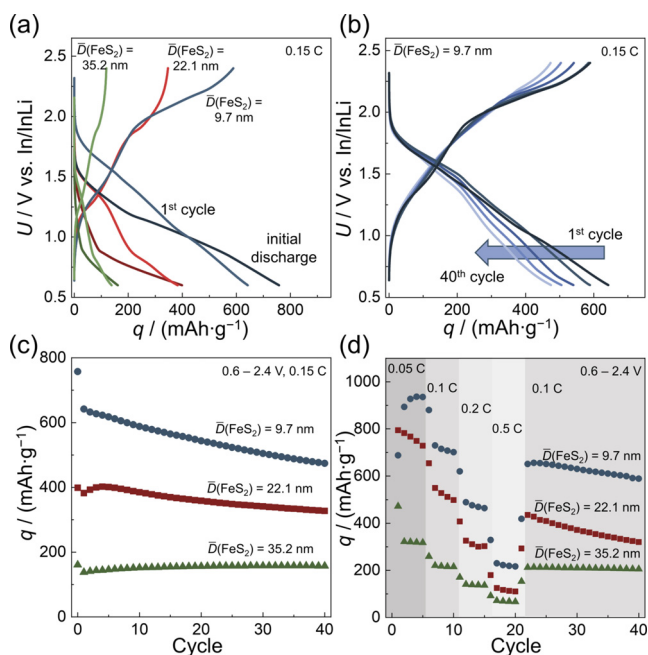


Figure 3. Influence of the FeS_2 particle size on performance of $\text{In}/\text{InLi}|\text{Li}_6\text{PS}_5\text{Cl}|\text{FeS}_2\text{-C-Li}_6\text{PS}_5\text{Cl}$ cells at 25 °C and an areal FeS_2 loading of 3.8 mg cm^{-2} in the cathode composite. C-rates were calculated based on four electron reductions of FeS_2 ($0.1 \text{ C} = 340 \mu\text{A cm}^{-2}$). While similar characteristics regarding the irreversibility of the initial discharge are observed in U-q plots, larger FeS_2 particles lead to lower capacities in the initial discharge and following first cycle (a). Despite the irreversible reduction of FeS_2 in the initial discharge, long-term cyclization performance suffers only from a gradual capacity fade over 40 cycles, shown exemplary for the cell with an average FeS_2 nanoparticle size of 9.7 nm (b). In direct comparison of long-term cyclization performance, the highest discharge capacities are obtained for a FeS_2 particle size of 9.7 nm (c). A similar trend is found for cyclization at different rates (d). Impedance spectra of the cells shown in (a) and (c) recorded prior to cycling can be found in the Supporting Information.

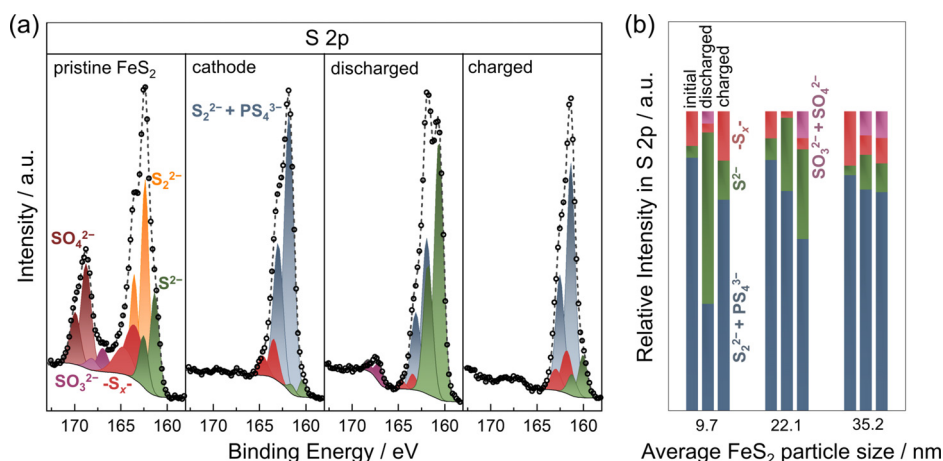


Figure 4. X-ray photoemission sulfur detail spectra of pristine FeS₂ nanoparticles (average particle sizes $\bar{D}$ of 9.7 nm) and FeS₂-C-Li₆PS₅Cl cathodes composites (a). A spectrum with multiple contributions is observed for as-synthesized FeS₂ particles. After addition of carbon black and Li₆PS₅Cl, the solid electrolyte and FeS₂ contributions to the sulfur signal overlap. An increasing intensity of reduced species indicates sulfur reduction upon cell discharge, reoxidized in the subsequent charge. By visualizing the changes in relative intensity contributions to the S 2p spectra upon cycling, a clear influence of FeS₂ particle size on the extent of sulfur cycling is highlighted (b). Values of relative intensities in S 2p as well as P 2p detail spectra are also shown in the (Supporting Information). This trend can be interpreted as improved sulfur utilization for small FeS₂ particle sizes.

chemical mechanisms involve the sulfur species. This suggests a degree of oxidative solid electrolyte degradation,^[17] which however seems to be independent of particle size and hence surface area of the employed FeS₂ particles. Therefore, the more pronounced sulfur redox behavior that can be found when using the smallest sizes FeS₂ nanoparticles suggests that more FeS₂ is electrochemically addressed and converted (see Figure 4b).

To exploit the remarkable theoretical capacity of conversion-type electrode materials in competitive solid-state batteries, performance bottlenecks such as low utilization of active materials and poor cycling efficiencies must be overcome. In this work, we used FeS₂ as a model-type conversion cathode for solid-state Li-ion storage due to its facile synthesis and high theoretical capacity. FeS₂ nanoparticles with three different size distributions were synthesized and characterized. The influence of the size distribution of FeS₂ on the solid-state battery performance was evaluated for In/InLi | Li₆PS₅Cl | FeS₂-C-Li₆PS₅Cl cells. A higher capacity and better rate capability were obtained for smaller particle sizes that are unfortunately also accompanied by faster capacity fading. The higher capacity and better rate capability is likely caused by the fact that more active material can be addressed due to the higher surface to volume ratio and the shorter Li⁺ diffusion pathways inside the FeS₂ nanoparticles. Nevertheless, this higher surface to volume ratio provides more interfacial area for competing decomposition reactions and more capacity fading.

Overall, this work highlights the potential of FeS₂ as conversion-type cathode material and especially the high relevance of using nanoscale conversion materials in solid state batteries. It further shows that, similar to solid-state batteries with oxide-based cathode active materials,^[33] par-

ticle size distribution of the cathode active materials also matters significantly in conversion-type solid-state batteries.

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Conflict of Interest

The authors declare no conflict of interest.

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