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Pyrite (FeS$_2$) Nanocrystals as Inexpensive High-Performance Lithium-Ion Cathode and Sodium-Ion Anode Materials

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ABSTRACT. In light of the impeding depletion of fossil fuels and necessity to lower carbon dioxide emissions, economically viable high-performance batteries are urgently needed for numerous applications ranging from electric cars to stationary large-scale electricity storage. Due to its low raw material cost, non-toxicity and potentially high charge-storage capacity pyrite (FeS$_2$) is a highly promising material for such next-generation batteries. In this work we present the electrochemical performance of FeS$_2$ nanocrystals (NCs) as lithium-ion and sodium-ion storage materials. First, we show that nanoscopic FeS$_2$ is a promising lithium-ion cathode material, delivering a capacity of 715 mAh g$^{-1}$ and average energy density of 1237 Wh kg$^{-1}$ for 100 cycles, twice higher than for commonly used LiCoO$_2$ cathodes. Then we demonstrate, for the first time, that FeS$_2$ NCs can serve as highly reversible sodium-ion anode material with long cycling life. As sodium-ion anode material, FeS$_2$ NCs provide capacities above 500 mAh g$^{-1}$ for 400 cycles at a current rate of 1000 mAg$^{-1}$. In all our tests and control experiments, the performance of chemically synthesized nanoscale FeS$_2$ clearly surpasses bulk FeS$_2$ as well as large number of other nanostructured metal sulfides.

High-performance batteries are increasingly needed for numerous applications such as portable electronics, electric cars or stationary storage systems in tandem with renewable sources of electrical energy. Due to their high energy density lithium-ion (Li-ion) batteries (LIBs) are often considered the storage system of choice for such applications. However, in the light of limited abundance and the thereby constantly increasing costs of Li-salts, there is growing interest to develop conceptually identical sodium-ion (Na-ion) batteries (SIBs) as a potentially less expensive alternative for large-scale applications. Importantly, technology transition from LIBs to SIBs will require not only a (rather obvious) replacement of Li-ions with Na-ions, but also choosing electrode materials composed exclusively of comparably abundant elements. Herein we draw reader’s attention to pyrite (FeS$_2$) as a promising low cost, non-toxic rechargeable electrode material for both LIBs and, for the first time, also for SIBs.

The quest for new electrode materials is primarily driven by the need to increase the energy density. The latter, in turn, is a product of charge storage capacity and voltage of operation. FeS$_2$ has a high theoretical specific charge-storage capacity of 894 mAh g$^{-1}$, assuming full lithiation/sodiation forming Li$_2$S/Na$_2$S+Fe. With these appealing attributes, FeS$_2$ is already in use as cathode material in commercial primary (non-rechargeable) Li-ion cells produced, for instance, by Energizer. Yet the development of secondary (rechargeable) LIBs with FeS$_2$ has been hampered by the poor reversibility of its lithiation/delithiation at room temperature. So far, only several reports have dealt with FeS$_2$ as a cathode material in secondary LIBs. For instance, Li et al. demonstrated FeS$_2$ nanooctahedra with a capacity retention of 495 mAh g$^{-1}$ after 50 cycles at 0.5C-rate (1C is current density of 894 mA g$^{-1}$). Very little work has so far concerned mechanisms of room-temperature sodiation of FeS$_2$, and high-capacity Na-ion storage, at high current densities and long-cycling life are still to be demonstrated.

In this study our aim was to enhance the reaction kinetics and reversibility of Na-ion and Li-ion storage using nanostructured FeS$_2$. Starting with inexpensive solution-phase chemical synthesis of nanosized FeS$_2$ particles, we systematically studied the performance of nano-FeS$_2$ as LIB and SIB electrode material and compared our results with bulk FeS$_2$. We find that owing to shorter diffusion path lengths for both electrons and ions, the nanoscopic counterpart exhibits highly reversible insertion of Li$^+$ and Na$^+$ ions, with near theoretical capacities. The corresponding voltage profiles indicate that nano-FeS$_2$ has great potential a cathode material for LIBs and as anode material for SIBs. As LiB cathode, FeS$_2$ NCs exhibit outstanding capacities of 720 and 600 mAh g$^{-1}$ after 50 cycles at current densities of 200 or 1000 mAg$^{-1}$, respectively. Further, using FeS$_2$ NCs for the first time as anode material in SIBs, we report high cycling stability with capacities of >500 mAh g$^{-1}$ for 400 cycles at a high current density of 1000 mAg$^{-1}$, making FeS$_2$ NCs one of the best performing SIB anodes identified so far.

The mechanism of lithiation and delithiation of FeS$_2$ has been established as:

\[
\begin{align*}
\text{FeS}_2 + 2\text{Li}^+ + 2e^- &\rightarrow \text{Li}_2\text{FeS}_2 \\
\text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2e^- &\rightarrow 2\text{Li}_2\text{S} + \text{Fe} \\
\text{Fe} + 2\text{Li}_2\text{S} &\rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2e^- \\
\text{Li}_2\text{FeS}_2 &\rightarrow \text{Li}_{2x}\text{FeS}_2 + x\text{Li}^+ + xe^- \quad (0.5 < x < 0.8) \\
\text{Li}_{2x}\text{FeS}_2 &\rightarrow \text{FeS}_2 + (2-y)\text{S} + (2-x)\text{Li}^+ + (2-x)e^- \\
\end{align*}
\]

More specifically, the final oxidation step was proposed to yield orthorhombic Fe$_2$S$_2$ and pyrrhotite Fe$_7$S$_6$ (Equation 6).
Li$_{2}$FeS$_{2}$ → 0.8ortho-FeS$_{2}$ + 0.2FeS$_{8/7}$ + 0.175S + (2-x)Li$^+$ + (2-x)C$^-$ \hspace{1cm} (6)

With nanostructured active materials, not only does the reaction kinetics improve, but also the instabilities caused by the effects of large volume changes might be mitigated.\textsuperscript{26-47} For instance, for the full sodiation of FeS$_2$ to Na$_2$S and Fe the volumetric expansion can reach 280\% based on the difference in the molar volumes between the initial (FeS$_2$) and the final (Fe, Na$_2$S) phases according to \%

\[ \Delta V = 100 \times \frac{2 \times V_m(Na_2S) + V_m(Fe) - V_m(FeS_2)}{V_m(FeS_2)} \]

Analogously, the lithiation of FeS$_2$ to Li$_x$S and Fe leads to volume changes of up to 160\% or, in other words, an increase of the volume by the factor of 2.6.

Figure 1. Synthesis and characterization of FeS$_2$ NCs: (a) reaction scheme; (b) transmission electron microscopy (TEM) images; (c) X-ray diffraction (XRD) pattern indexed to pure-phase pyrite FeS$_2$ (ICDD database, PDF No.: 00-071-2219; space group N205, Pa3, a = 5.4179 Å); (d) schematic representation of the unit cell of pyrite FeS$_2$.

We prepared FeS$_2$ NCs via adaptation of the synthesis proposed by Li et al.\textsuperscript{28} In short, FeCl$_2$ and elemental S were mixed at 120 °C in oleylamine (OLA), acting as both solvent and surfactant, and reacted at 220 °C for two hours delivering highly crystalline 50-100 nm large FeS$_2$ NCs (Figure 1) with high reaction yield (99\%). No traces of unreacted reagents, marcasite FeS$_2$ or other iron sulfides of different stoichiometry (FeS or Fe$_2$S$_3$) could be detected. Moreover, no traces of oxides were observed, indicating that FeS$_2$ NCs can be readily handled in air. Based on the low-cost, inexpensive and environmentally benign precursors, scalable heating-up reaction, and recyclable coordinating solvent (OLA), this synthesis can be readily implemented on industrial scale as well.

The electrochemical properties of the as-synthesized FeS$_2$ NCs were investigated in airtight coin type half-cells using either elemental lithium or sodium as both counter- and reference electrodes. The remaining surface-bound OLA molecules were removed from the NC surface by treatment with hydrazine, as commonly applied for colloidal quantum dots for improving their electronic connectivity.\textsuperscript{39} The removal of ligands was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Figure S1).

It should be noted that no changes in terms of size, shape or composition could be observed by TEM and XRD upon removal of residual OLA ligand (Figure S2) and after electrode preparation (Figures S3 and S4). All electrodes containing FeS$_2$ NCs were prepared by mixing the active material (64 wt\%) with carbon black (CB, 21\%) as conductive additive and with carboxymethylcellulose (CMC, 15\%) as a binder, forming a homogeneous aqueous slurry which was coated onto Cu-foil and dried. Loading of the active material was ~0.5 mg/cm$^2$, yielding thickness of ~15 μm. Fluoroethylene carbonate (FEC) was added to the electrolyte to improve the cycling stability.\textsuperscript{38, 50, 51} The results for measurements of FeS$_2$ NCs as cathode material in Li-ion half cells are shown in Figure 2. Cells were initially discharged to 0.02 V and then cycled in the potential range between 1.0 – 3.0 V. The capacities above the theoretical value for the first cycle can be explained by the irreversible formation of the solid electrolyte interface (SEI), seen also as low coulombic efficiency (CE), that is a ratio between charge and discharge capacity), of 75\% in the first cycle. Upon subsequent cycling at 200 mAg$^{-1}$ FeS$_2$ NCs deliver initial capacities close to the theoretical maximum with 800 mAhg$^{-1}$ and show only minor
capacity fading during cycling (Figure 2a). Namely, after 100 cycles of charging/discharging FeS₂ NCs still deliver 630 mAhg⁻¹ corresponding to capacity retention of 80%. In contrast, bulk FeS₂ shows both significantly lower initial capacities and much faster fading. Despite the fact that the average lithiation potential for FeS₂ NCs is moderately low - 1.73 V (for 1.0 – 3.0 V range, Figure 2c) or 2.0 V (for 1.5 – 3.0 V range) - the high capacities result in energy densities more than twice higher than of commercially established LiCoO₂ or LiFePO₄ (Figure 2b, Table 1). Even when the current is increased to 1000 mAg⁻¹, more than 600 mAhg⁻¹ can be retained for 50 cycles (Figure 2d). At all current rates CE is ≥99%. To our knowledge this excellent performance in terms of obtaining high capacities at high currents is unprecedented for FeS₂ as cathode in LIBs (for detailed comparison with literature, see Table S1). It should be noted that in the absence of FEC as electrolyte additive much poorer capacity retention was observed (Figure S5).

Table 1. Comparison of Li-ion cathodic performance of FeS₂ NCs, with commercial LiCoO₂ and LiFePO₄ materials. Energy density is calculated as a product of the specific capacity and average voltage during discharge. For Li-ion full cells the lack of Li in FeS₂ might be compensated by either electrochemical prelithiation of the material or using Li-containing anode materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Capacity in mAhg⁻¹</th>
<th>Potential (vs. Li/Li) in V</th>
<th>Energy Density in Whkg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS₂ NCs</td>
<td>715 (397)</td>
<td>1.73 (2.0)</td>
<td>1237 (794)</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>140</td>
<td>3.9</td>
<td>546</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>170</td>
<td>3.4</td>
<td>578</td>
</tr>
</tbody>
</table>

Contrary to LIBs, cycling of FeS₂ NCs as cathode material in Na-ion half cells delivers only approximately half the expected capacity and suffers from both faster capacity fading and poorer coulombic efficiency with values ranging from 98 to 96% (Figure S6). Although the performance of such FeS₂ NCs as cathode for SIBs is still superior to previous reports (for detailed comparison with literature, see Table S2),²³⁻²⁵ it shows a drastic difference between Li-ion and Na-ion chemistries. Considering that in case of Na-ion cells a much higher fraction of the charge storage capacity is gained at lower potentials (Figure S3b), galvanostatic cycling measurements in the range 0.02 – 2.5 V were carried out to analyze the applicability of FeS₂ NCs as an anode material. In particular, we find that FeS₂ NCs deliver capacities of 600 mAhg⁻¹ after 200 cycles at a relatively high current of 1000 mAg⁻¹, and capacity of 500 mAhg⁻¹ after 400 cycles (Figure 3a). After 600 cycles, FeS₂ NCs still deliver capacities of 410 mAhg⁻¹, corresponding to 50% of the initial capacity. In contrast electrodes composed of bulk FeS₂ show much lower capacities, presumably due to slower reaction kinetics. Furthermore, for FeS₂ NCs the CE increases from approximately 97% for the first 100 cycles to an average of 99% for the subsequent cycles demonstrating good reversibility of Na-ion storage. Addition of FEC to the electrolyte was found to be crucial, since cells without FEC showed extremely poor CE of 95 – 83% (Figure 3c). Moreover, cycling tests with limitation of the charge capacity to 500 mAhg⁻¹ were carried out to restrict the desodiation to lower potentials, which is a preferred scenario for the full cell as it will retain largest possible potential difference between the cathode and anode and hence the energy density. No capacity fading was observed for 500 cycles at current density of 1000 mAg⁻¹. In addition, electrodes with FeS₂ NCs can be cycled with a current rate as high as 5000 mAg⁻¹ and still deliver capacities above 600 mAhg⁻¹ for at least 50 cycles corresponding to a retention of 86% of the initial capacity (Figure 3d).

To elucidate the phase evolution during sodiation and desodation of FeS₂, ex-situ XRD measurements were carried out (Figure S7) at various stages of electrochemical cycling. Starting from the pristine pyrite structure of FeS₂, no intermediate crystalline phases were observed and no crystalline FeS₂ was restored during charging.

Table 3. Electrochemical performance of FeS₂ NCs tested as anode material for SIBs. a) Capacity retention for FeS₂ NCs and bulk FeS₂. b) Galvanostatic charge and discharge curves for FeS₂ NCs corresponding to the graph in a). c) Capacity retention for FeS₂ NCs cycled with the same conditions as in a) but without the addition of FEC to the electrolyte. d) Capacity retention for FeS₂ NCs cycled with 5000 or 1000 mAhg⁻¹. e) Capacity retention for FeS₂ NCs cycled with limitation of the charge capacity to 500 mAhg⁻¹. All batteries were measured in the 0.02 – 2.5 V potential range at a current of 1000 mAg⁻¹ unless noted otherwise. 1M NaClO₄ in propylene carbonate (PC) with 10% fluoroethylene carbonate (FEC) served as electrolyte in Na-ion half cells.

We acknowledge the possibility that crystalline intermediate phases exist, but cannot be detected due to very small crystallite domain size in the nanometer range. Based on the observed capacities close to the theoretical value of 894 mAhg⁻¹ and the aforementioned reports we assume that the sodiation of FeS₂ NCs leads to the formation of Na₂S involving most likely only amorphous phases according to the following mechanism:

\[
\text{FeS}_2 + 2\text{Na}^+ + 2\epsilon \rightarrow \text{Na}_2\text{FeS}_2
\]  

(7)

\[
\text{Na}_3\text{FeS}_2 + 2\text{Na}^+ + 2\epsilon \rightarrow 2\text{Na}_2\text{S} + \text{Fe}
\]  

(8)

Amorphous state during cycling may explain the apparently low kinetic restraints for fast charging/discharging and reduced...
mechanical stress upon expansion and contraction, similarly to our earlier observations with Sb NCs as Na-ion anode material.\textsuperscript{44}

![Figure 4](image)

**Figure 4.** Electrochemical performance of various metal sulfide NCs tested as anode material for SIBs. All batteries were measured in the 0.02 - 2.5 V potential range at a constant current of 1000 mAg\textsuperscript{-1}. 1M NaClO\textsubscript{4} in propylene carbonate (PC) with addition of 10 wt% of fluoroethylene carbonate (FEC) served as electrolyte.

Performance of FeS\textsubscript{2} compares very favorably with other metal sulfides reported up to date (for detailed comparison with literature, see Table S3). For the sake of fully objective and unbiased comparison, we thus have synthesized and carefully studied, under identical testing conditions, colloidal NCs of a vast variety of prime metal sulfide candidates for Na-ion storage, composed of earth-abundant elements, such as NiS\textsubscript{2}, CoS\textsubscript{2}, PbS, SnS, CuS, ZnS and Cu\textsubscript{2}ZnSnS\textsubscript{2} (see Figures 4 and S8). With the exception of SnS all of these sulfides had not been previously tested for Na-ion storage, judging from the available literature. Clearly, in comparison with all these sulfides, FeS\textsubscript{2} shows both higher initial capacity and better long-term cycling stability.

**Conclusions**

In conclusion, we identified and demonstrated a great potential of FeS\textsubscript{2} NCs as inexpensive, environmentally benign and, most importantly, high-energy-density and long-cycling electrode material for LIB cathodes and SIB anodes, outperforming bulk FeS\textsubscript{2} and other metal chalcogenide NCs under identical testing conditions. Cathodic Li-ion storage by FeS\textsubscript{2} NCs is characterized by high specific capacity of ≥630 mAhg\textsuperscript{-1} for 100 cycles (at a current of 200 mAg\textsuperscript{-1}), delivering more than twice the energy density of LiCoO\textsubscript{2} or LiFePO\textsubscript{4}. Anodic Na-ion storage exhibits even better overall performance, with capacities of ≥500 mAhg\textsuperscript{-1} retained after 400 cycles at a current density of 1000 mAg\textsuperscript{-1}. We note that we used very standard, thus possibly suboptimal for nanostructures testing conditions in terms of selected binder, electrolyte and (most simple) electrode formulation. Future work on FeS\textsubscript{2} as electrode material should focus on smart electrode engineering, involving recent specific for alloying or conversion nanostructured anodes developments such as design of three-dimensional nanoarchitectures or elaborate encapsulation of nanoparticles into conductive carbons.\textsuperscript{33-57}

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**Notes and references**

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FeS$_2$ nanocrystals are presented as high-performance lithium-ion cathode and sodium-ion anode materials with high cycling stability.