Dendritic nanostructured FeS$_2$-based high stability and capacity Li-ion cathodes†

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Here we show that dendritic architectures are attractive as the basis of hierarchically structured battery electrodes. Dendritically structured FeS$_2$, synthesized via simple thermal sulfidation of electrodeposited dendritic α-Fe, was formed into an electrode and cycled vs. lithium. The reversible capacities of the dendritic FeS$_2$ cathode were 560 mA h g$^{-1}$ at 0.5C and 533 mA h g$^{-1}$ at 1.0C after 50 cycles over 0.7–3.0 V. Over 0.7–2.4 V, where the electrode is more stable, the reversible capacities are 348 mA h g$^{-1}$ at 0.2C and 179 mA h g$^{-1}$ at 1.0C after 150 cycles. The good cycling performance and high specific capacities of the dendritic FeS$_2$ cathodes are attributed to the ability of a dendritic structure to provide good ion and electron conducting pathways, and a large surface area. Importantly, the dendritic structure appears capable of accommodating volume changes imposed by the lithiation and delithiation process. The presence of a Li$_2$-FeS$_2$ phase is indicated for the first time by high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) electron energy loss spectroscopy (EELS). We suspect this phase is what enables electrochemical cycling to possess high reversibility over 0.7–2.4 V.

Introduction

In the quest for improved lithium-ion batteries (LIBs), considerable effort has been made to enhance the electrochemical properties of cathode materials.¹ Along with development of new material systems,²–⁵ an increasing number of groups are paying attention to the relationship between the electrochemical properties and the morphology of the active material.⁶,⁷ Nanostructuring offers a number of advantages, including shorter solid state ionic and electron transport pathways, and an increased contact area with the electrolyte, which improves the rate performance.⁸–¹¹ However, this increased surface area can also lead to an increase in solid electrolyte interphase formation, which may be detrimental to the cycle life. Additionally, maintaining both good electron and ion transport pathways in a nanostructured system can be challenging.

It would provide a significant advantage if a hierarchical structure which exhibits a stable nanostructure and a robust macrostructure could be synthesized in a single step. Such a structure would provide a large number of active sites, a stable framework, and short diffusion lengths.¹²,¹³ Due to the advantages of such a structure, a wide range of hierarchically structured electrodes, which have exhibited excellent cycling performances and high reversible capacities, have been synthesized and studied,¹⁴,¹⁵ including hierarchical systems based on metal oxides,¹⁶–¹⁸ LiFePO$_4$ (ref. 21 and 22) and Li$_4$Ti$_5$O$_12$.¹⁹ In cases such as Si, the hierarchical structure is also important in preventing volume change induced degradation during lithiation and delithiation.²⁰,²¹ Notably, dendritic nanostructures, which have been widely studied in other fields, prior to this work, have not been considered for use as electrode materials for Li ion batteries.

Due to their high theoretical capacities, metal sulfides including SnS$_2$,²⁶–²⁸ MoS$_2$,²⁹–³¹ CuS$_2$,³² and FeS$_2$,³³ CoS$_2$,³⁴ and Ni$_3$S$_2$ (ref. 36) are considered promising electrode materials. FeS$_2$ (pyrite) has in particular been commercialized as a lithium battery cathode due to its high theoretical capacity (894 mA h g$^{-1}$), earth abundance, environmentally benign nature and high temperature stability.²⁴–⁴⁰ With only a few exceptions however, pyrite has shown poor cyclability owing to its low electrical conductivity and limited reversibility, limiting its use to primary batteries.⁴¹,⁴² If these problems can be overcome, FeS$_2$ will be a much more promising cathode material for next generation lithium-ion batteries.
The pure iron pyrite nanowire cathode materials synthesized by Song et al.\(^\text{39}\) retained a discharge capacity of 350 mA h g\(^{-1}\) after 50 cycles and 0.1C, possibly because of the improved reaction kinetics provided by the nanostructure. Liu et al.\(^\text{37}\) coated a carbon layer on octahedral FeS\(_2\) nanocrystallites to enhance electrical conductivity and structure stability, and this system exhibited a capacity retention of 495 mA h g\(^{-1}\) after 50 cycles at 0.5C. Wang et al.\(^\text{41}\) reported hierarchically structured hollow FeS\(_2\) microspheres which showed reasonable capacity and cycling performance (392.7 mA h g\(^{-1}\) after 30 cycles at 1C). All of these works emphasized the importance of nanostructuring for improving the electrochemical properties of pyrite cathodes. Here, we describe a facile self-assembly route for preparing dendritically structured pyrite-based Li-ion cathodes. These dendritic FeS\(_2\) composite cathodes exhibit high specific capacities and good cycling performance in the voltage window of both 0.7–2.4 V and 0.7–3.0 V. The Li\(_2\)S–FeS\(_2\) phase was observed by high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) mode. Identification of this phase may enable further understanding of the lithiation/delithiation mechanism of FeS\(_2\).

**Experimental section**

1 **Synthesis of the hierarchically structured FeS\(_2\)**

Ferrous heptahydrate (FeSO\(_4\)·7H\(_2\)O, Sigma Aldrich) was used to synthesize the dendritically structured \(\alpha\)-Fe by an electric-field-induced and electrochemical reduction method.\(^\text{42}\) The hierarchically structured dendritic pyrite was obtained via thermal sulfidation of the as-synthesized dendritic \(\alpha\)-Fe at 450 °C for 4 hours with a heating and cooling rate of 15 °C per minute under a continuous argon gas flow. Elemental sulfur (99.5–100.5%, Sigma Aldrich) was placed at the edge of the furnace, where it reached about 140 °C and formed a melt. The resulting sulphur vapour was carried by the argon gas flow over the dendritic nanostructured \(\alpha\)-Fe.

2 **Material characterization**

Sample composition and microstructure were determined by: X-ray diffraction (Philips X’pert XRD system with Cu K\(\alpha\) radiation, \(\lambda = 0.15418\) nm); scanning electron microscopy and energy dispersive spectroscopy (Hitachi S-4700 SEM, EDS); transmission electron microscopy and high-resolution transmission electron microscopy (JEOL 2100 cryo, TEM and HRTEM); and electron energy loss spectroscopy (EELS) during scanning transmission electron microscopy (JEOL, 2010F STEM). Cycling of TEM and STEM-EELS samples were performed by dispersing the dendritic nanostructured FeS\(_2\) into ethanol, placing a couple of droplets on a copper grid with a carbon support film (EMS Acquisition Corp), covered by an identical copper grid and dried 2 h at 80 °C. The two grids were held by a toothless clamp and used as a cathode in a bottle cell. 1 M lithium hexafluorophosphate (LiPF\(_6\)) in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (2 : 1 : 2 in volume) was used as the electrolyte. 10 wt% fluoroethylene carbonate (FEC, Sigma Aldrich) was added to the electrolyte. The counter electrode is lithium foil (Alfa Aesar). After 7 charge/discharge cycles using about 0.2C rates between 0.7–2.4 V, the samples were removed from the electrolyte, and immersed into dimethyl carbonate (DMC) solvent for 30 min to remove the rest of electrolyte. The copper grids were taken out of the glove box, and immediately transferred to the TEM column for analysis.

3 **Fabrication of the composite cathode and electrochemical measurements**

Composite electrodes were fabricated through mixing of the as-synthesized dendritic FeS\(_2\), carbon black (Super P Conductive, Alfa Aesar), and poly(vinylidene fluoride) (PVDF, MTI) binder (65 : 25 : 15 weight ratio) using a homogenizer (GLH-115, OMNI International) for 15 min in N-methylpyrrolidone (NMP, MTI). The resulting slurry was printed onto a conductive carbon-coated copper foil current collector (MTI) with an average FeS\(_2\) active material mass loading of 1–1.5 mg cm\(^{-2}\). Then, the composite electrodes were dried for 10 h at 120 °C. 9.5 mm diameter electrode disks were punched and then dried at 100 °C in a vacuum oven for 12 h before cell assembly.

Two-electrode battery-type Swagelok cells were used to test the electrochemical properties of the composite electrode on a VMP3 (Bio-Logic) potentiostat. Cyclic voltammetry (CV) was performed between 0.7–2.4 V and 0.7–3.0 V at a scan rate of 0.2 mV s\(^{-1}\). Electrochemical impedance spectroscopy (EIS) was performed on Swagelok cells after various cycle numbers at 2.4 V over a frequency range of 100 kHz to 10 mHz with an AC amplitude of 5.0 mV. The cells were kept at 2.4 V for 4 h, and allowed to rest for 4 h before taking EIS measurements.

**Results and discussion**

Fig. 1a–c shows scanning electron microscopy (SEM) images of the as-synthesized FeS\(_2\). The dendritic FeS\(_2\) particles are 8 to 15
µm in length and 4 to 6 µm in width, and possess a fine nanostructure on the branches and tips (in Fig. 1c). Energy dispersive spectroscopy (EDS) (Fig. S1†) indicates the atomic ratio of S to Fe is 2:1. All peaks in the X-ray diffraction (XRD) pattern (in Fig. 1d) can be indexed to pure cubic FeS₂ (JCPDS no. 65-7643, a = 0.5404 nm). No impurities such as elemental Fe, elemental S or marcasite were detected.

The electrochemical performance of as-synthesized dendritic nanostructured FeS₂ was studied in two-electrode elemental S or marcasite were detected. 0.7

150 cycles, exceeding that reported for pyrite nano-wires over the voltage range of 0.7–2.4 V and (c) 0.7–3.0 V; and consecutive rate capability (e) from 0.2C to 3C over 0.7–2.4 V and (d) 0.7–3.0 V.

Fig. 2 Cycling stability of the dendritic FeS₂ composite electrodes (a) between 0.7–2.4 V at 0.2C, 0.5C and 1C, and (b) between 0.7–3.0 V at 0.5C and 1C; voltage–capacity curves in (c) 0.7–2.4 V and (d) 0.7–3.0 V range; and consecutive rate capability (e) from 0.2C to 3C over 0.7–2.4 V and (f) from 0.2C to 2C over 0.7–3.0 V.

Fig. 3 Electrochemical properties of the dendritic FeS₂ composite cathode at different cycle. CV at a scan rate of 0.2 mV s⁻¹ over (a) 0.7–2.4 V and (c) 0.7–3.0 V; differential capacity versus voltage over (b) 0.7–2.4 V and (d) 0.7–3.0 V at 0.2C.

Due to the relatively slow diffusion of Li⁺ into FeS₂, reactions (1) and (2) proceed simultaneously at room temperature (≤30 °C), and thus only single broad reduction peak appears. The oxidation peak includes the reactions,\(^6\):

FeS₂ + 2Li⁺ + 2e⁻ → Li₂FeS₂
(1)
Li₂FeS₂ + 2Li⁺ + 2e⁻ → 2Li₂S + Fe⁰
(2)

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2Li₂S + Fe⁰ → Li₂FeS₂ + 2Li⁺ + 2e⁻  
Li₂FeS₂ → Li₂₋ₓFeS₂ + xLi⁺ + xe⁻ (0 < x < 0.8)  

Generally, the hexagonal Li₂₋ₓFeS₂ phase begins to decompose into ortho-FeS₂ above 2.4 V as described in reaction (5)\(^{18,48}\)

Li₂₋ₓFeS₂ → 0.8ortho-FeS₂ + 0.2FeS⁸/⁷ + 0.175S + (2−x)Li⁺ + (2−x)e⁻  

leading to another oxidation near 2.6 V (see Fig. 3c). Because the electrode does not fully revert to FeS₂ during oxidation, even above 2.4 V, the CE of the first few cycles is low.

After the first cycle, subsequent cycles between 0.7–2.4 V show a stable redox couple at 1.35 and 2.15 V corresponding to reactions (2), (3) and (4), respectively. The differential capacity versus voltage curves show that the redox reactions proceed at 1.50 and 1.85 V (Fig. 3b) when cycling at 0.2 C. The CV curves of the composite cathode show two stable redox reactions during subsequent cycles when cycling over 0.7–3.0 V. In differential capacity curves (Fig. 3d), the peak at 2.50 V is from reaction (5), while the small broad reduction peak at 2.10 V corresponds to reduction of ortho-FeS₂, S and lithium sulphides.\(^{46}\) The S and lithium sulphides are difficult to decompose and dissolve more easily in the electrolyte, which lead to the low reversibility of reaction (5), and probably is the main reason for the rapid capacity fade during cycling between 0.7–3.0 V.\(^{38,49}\) A 3.0 V cut off voltage does provide greater capacity, but also results in fast capacity fade.

We suggest the FeS₂ electrochemical performance over 0.7–2.4 V can be attributed to the high reversibility of the intermediate Li₁₋ₓFeS₂ and dendritic structure of FeS₂ which provides a large surface area,\(^{50,51}\) a good electron and ion transport network, and a mechanically robust structure (note, while we cannot extract the active material from a cycled electrode, as Fig. 4a shows, the dendritic structure is retained with cycling). The dendritic structure increases both the reaction area between the active materials and the electrolyte, and shortens the solid-state Li ion diffusion length. These are important parameters at high charge/discharge rates.

As result above, the dendritic nanostructured FeS₂ shows better cycling performance between 0.7 and 2.4 V than between 0.7 and 3.0 V, because of the high reversibility of the intermediate Li₁₋ₓFeS₂ phase. To study the Li ion lithiation/delithiation process and confirm the formation of Li₁₋ₓFeS₂, high-resolution transmission electron microscopy (HRTEM) images and scanning transmission electron microscopy energy loss spectroscopy (STEM-EELS) analyses in spot mode were performed on the dendritic FeS₂ after 7 cycles at low charge/discharge rates (about 0.2 C). The voltage vs. time curve (in Fig. S2†) shows clear charging/discharging conversion plateaus. Fig. 4a shows TEM images of cycled dendritic FeS₂ after the final charging to 2.4 V, indicating that the dendritic structure is retained after cycling. HRTEM images in Fig. 4b show a clear phase boundary on the edge of the dendritic FeS₂. The majority of inner part of the sample shows a 0.271 nm lattice spacing, corresponding to (200) crystal planes of cubic FeS₂. Another HRTEM image after cycling, as well as a HRTEM image before cycling tests is shown in Fig. S3.† These images indicate that after a small number of cycles, the inner parts of the dendrite are still cubic FeS₂ that has not reacted with Li. The lattice spacing near the surface is about 0.60 nm, very close to the theoretical value for the (001) planes in hexagonal-close-packed Li₁FeS₂. The fast Fourier transform (FFT) of the image, shown in top right of Fig. 4b, was taken from the outlined regions in the image and can be indexed to the [110] zone axis of the Li₁FeS₂ phase (crystal data adopted from the International Crystal Structural Database (ICSD #68380)). A simulated electron diffraction pattern of the Li₁FeS₂ phase along the [110] zone axis using the CrystalMaker™ software (right bottom inset in Fig. 4b) is in good agreement with the experimental FFT pattern, suggesting that the outside layer of the structure is the Li₁FeS₂ phase. Due to the low cut off voltage of 0.7 V, lithiation is incomplete, and the material is likely to be Li₁₋ₓFeS₂, which possess the same crystal structure as Li₁FeS₂.

Fig. 4d shows the EELS spectra taken from the body (position A) and edge (position B) of cycled dendritic FeS₂, as indicated in the STEM high angle annular dark field (HAADF) image in Fig. 4c. After background subtraction, a clear wide peak at about 63.5 eV is observed at the edge of cycled dendritic FeS₂, which corresponds to the Li K-edge.\(^{52}\) The corresponding peak is not found in the intact inner region, indicating that only the outside part of dendrite is lithiated. Our TEM data provide direct evidence that the lithium ions are incorporated into the dendritic FeS₂ nanostructure, resulting in the formation of the Li₁₋ₓFeS₂ phase during the lithiation process.

Besides of the high reversible intermediate Li₁₋ₓFeS₂ phase, the robust dendritic structure is the other key factor of dendritic FeS₂’s good cycling properties. The architecture of FeS₂ provides
presumably by resulting in a thin and dense SEI. However, we still observe a steady capacity fade, indicating probably that a more stable SEI is still required, and that a robust artificial SEI, for example such as one formed via atomic layer deposition, might be required to stabilize the dendritic structure over many cycles. We postulate that the Li$_2$FeS$_2$ phase, which was observed by HRTEM and STEM-EELS, is one reason that the dendritic FeS$_2$ shows better cycling performance over 0.7–2.4 V than over 0.7–3.0 V, where electrolyte-soluble products are formed.

**Conflicts of interest**

There are no conflicts to declare.

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**References**