# Supporting Information

**Dendritic Nanostructured $FeS_2$-Based High Stability and Capacity Li-ion Cathodes**

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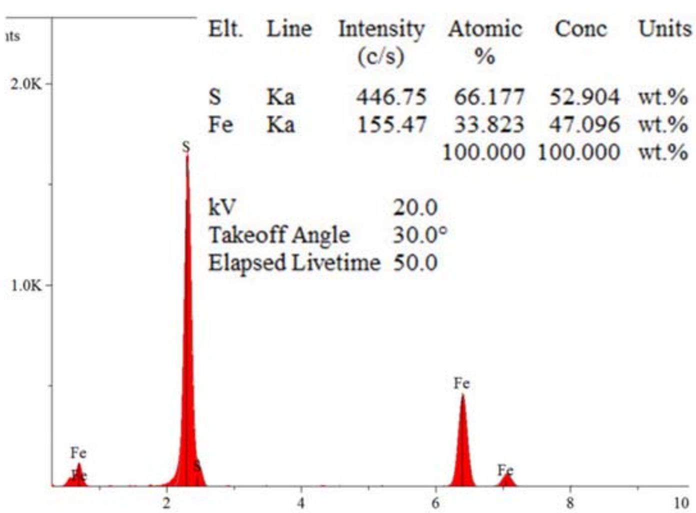


**Figure S1.** EDS obtained from the as-synthesized dendritic $FeS_2$

**Table S1.** Electrochemical performance of this work and other $FeS_2$-based Li-ion cathodes.

| Electrode | Cut off voltage (V) | Capacity (mAh/g) | Cap. retention@50 cycles (%) |
|---|---|---|---|
| (PNA) -$FeS_2$ [45] | 1.0-3.0 | 729@0.1C | 64 |
| $FeS_2$/$TFSI^-$-based IL [39] | 1.0-3.0 | 610@0.1C | >80 |
| $FeS_2$@C porous nanooctahedra [37] | 1.0-3.0 | 509@0.5C | 90 |
| FeS2 nanowires [38] | 1.1-2.4 | 409@0.1C | 85 |
| dendritic $FeS_2$ (this work) | 0.7-3.0 | 796@0.5C | 70 |
| dendritic $FeS_2$ (this work) | 0.7-2.4 | 491@0.5C | 85 |

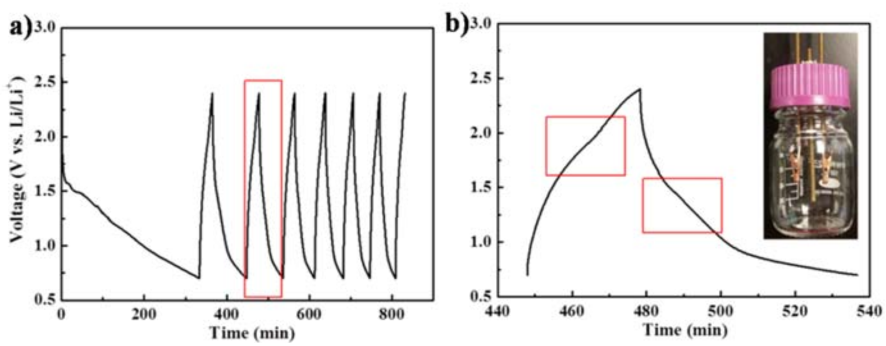


**Figure S2.** a) The voltage vs. time curve of the hierarchical dendritic $FeS_2$ cycled 7 times at about 0.2 C. b) The voltage vs. time curve of $2^{nd}$ cycle. The insert is the bottle cell used for TEM sample cycling.

Figure S2b shows charging/discharging conversion plateaus, indicating that the lithium ion lithiation and delithiation proceeds. After 7 cycles, the dendritic samples on the copper grid were immediately characterized by TEM and HRTEM.

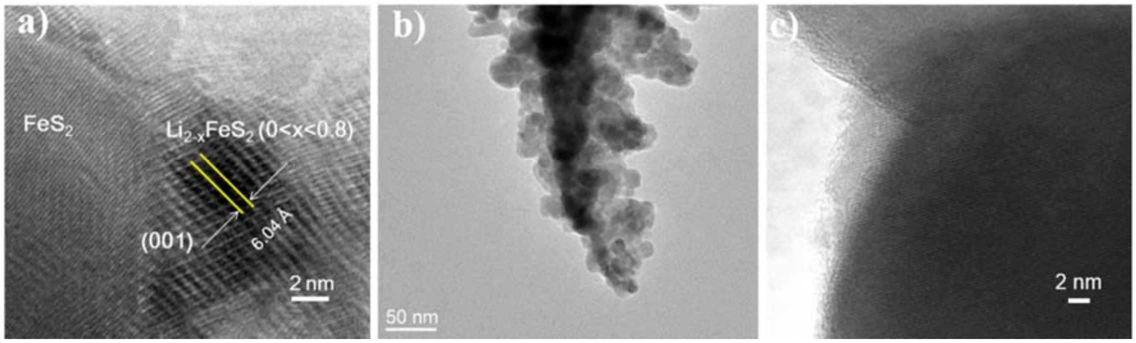


**Figure S3. a)** HRTEM image of dendritic $FeS_2$ after 7 cycles at about 0.2 C, b) TEM image of dendritic $FeS_2$ before cycling tests, and c) HRTEM image of dendritic $FeS_2$.

HRTEM image of dendritic $FeS_2$ after 7 cycles at about 0.2 C in Figure S3a also shows a clear phase boundary between $FeS_2$ and $Li_{2-x}FeS_2$ and lattice spacings of the (001) planes of the $Li_2FeS_2$. These HRTEM images also confirm the presence of $Li_{2-x}FeS_2$ as an intermediate phase during cycling. TEM image of $FeS_2$ before cycling (Figure S3b) confirms the dendritic structure is present in the as-synthesized material. HRTEM image of an edge of the dendritic $FeS_2$ shows the lattice fringes of cubic $FeS_2$ (Figure S3c).

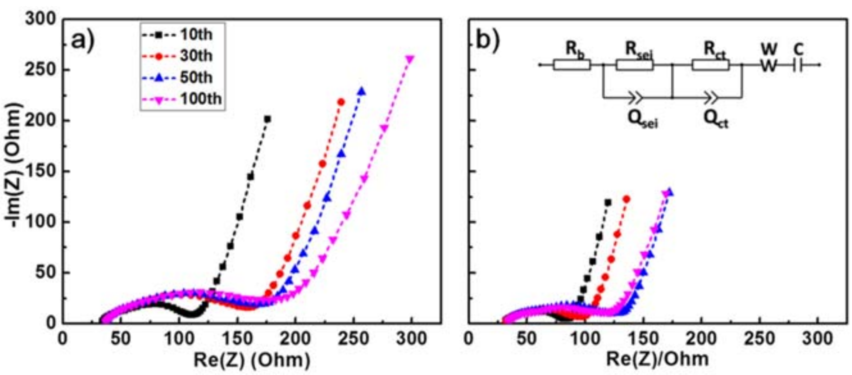


**Figure S4.** EIS of the dendritic $FeS_2$ composite electrode in a) FEC-free and b) 10 wt% FEC-containing electrolyte at room temperature.

**Table S2.** Fitted results from EIS in FEC-free and FEC-containing electrolyte.

| Cycle number | Electrolyte without FEC | | | Electrolyte + 10wt% FEC | | |
|---|---|---|---|---|---|---|
| | $R_b$ /ohm | $R_{sei}$ /ohm | $R_{ct}$ /ohm | $R_b$ /ohm | $R_{sei}$ /ohm | $R_{ct}$ /ohm |
| 10 | 33.22 | 66.41 | 11.00 | 29.83 | 28.84 | 23.31 |
| 30 | 35.42 | 96.96 | 20.07 | 29.70 | 39.32 | 22.75 |
| 50 | 35.11 | 102.9 | 19.53 | 31.03 | 64.90 | 26.67 |
| 100 | 35.35 | 121.6 | 20.02 | 31.00 | 48.79 | 27.93 |

Electrochemical Impedance Spectroscopy (EIS) was used to study the electrode properties from 100 kHz to 10 mHz at room temperature; the results are shown in Figure S4 and Table S2. Figures S4a and S4b show EIS of the $FeS_2$ cathode discharged to 2.4 V in the electrolyte with and without FEC after increasing cycle numbers (cycled at 1C). The EIS curves can be analyzed using the equivalent circuit model included in Figure S4b. $R_b$ represents the intercept on the Re(Z) axis, which comes from the resistance of the electrolyte, separator, and electrical contacts; $R_{sei}$ corresponds to the depressed semicircle in the intermediate frequency range, which is related to the Li-ion migration resistance through the solid-electrolyte interphase (SEI) film formed on the electrode and/or another coating layer; $R_{ct}$, the second semicircle, indicates the faradic charge transfer resistance. The inclined line in the low frequency representes the Warburg impedance, which is associated with Li-ion diffusion in the $FeS_2$.[1] The auto fit values of each element from the EC-lab software are given in Table S2. Both $R_b$ and $R_{ct}$ remain similar after adding 10 wt% FEC into the electrolyte. However, $R_{sei}$ changes significantly. In the FEC-free electrolyte, $R_{sei}$ is 66.41 ohm after $10^{th}$ cycle, and increases quickly with the cycle number (121.6 ohm at the $100^{th}$ cycle). This indicates that there is a continuously growing undesirable SEI layer on the cathode surface. $R_{sei}$ in the FEC-containing electrolyte is 28.84 ohm at the $10^{th}$ cycle, reaches 64.9 ohm at $50^{th}$ cycle, and then is largely unchanged through at least the $100^{th}$

cycle, confirming that the added FEC contributes to forming a thinner and more stable SEI. A thin and stable SEI both enhances the cathode cycling performance, and probably helps to retain the dendritic $FeS_2$ structure.[2, 3]

**References:**


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2. V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching and D. Aurbach, *Langmuir*, 2012, **28**, 965-976.
3. S. S. Zhang, *J. Power Sources*, 2006, **162**, 1379-1394.