A General Method to Fabricate Free-Standing Electrodes: Sulfonate Directed Synthesis and their Li⁺ Storage Properties

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Figure S1. (a) FESEM image of the sulfonated HIPE polymer at high magnification; (b) FESEM image of the sulfonated HIPE polymer at low magnification.



Figure S2. Cross-sectional view FESEM images of the CF/Fe₃O₄-FS-2 electrode



Figure S3. (a) FESEM image of the CF/Fe₃O₄-FS-1 composite; (b) FESEM image of the CF/Fe₃O₄-FS-5 composite; (c) FESEM images of the CF/Fe₃O₄-W/O-N at low and high magnifications (inset image); (d) FESEM images at low and high magnifications (inset) of CF/Fe₃O₄-W/O-PVA.



Figure S4. (a) Raman spectra of various CF/Fe_3O_4 -FS composites; (b) Nitrogen adsorption-desorption isotherms of CF/Fe_3O_4 -FS-2 and corresponding pore size distribution (inset).

As shown in Figure S4a, the Raman spectra of all the composites present two distinguishable peaks at about 1348 cm⁻¹ (D band) and 1590 cm⁻¹(G band). The former peak associates with in-plane A_{1g} zone-edge mode of the graphite structure due to the lack of long range order in amorphous and quasi-crystalline forms of carbon materials; while the latter band corresponds to the E_{2g} mode (stretching vibrations) in the basal plane of the crystalline graphite. The peak intensity ratio between D- and G-bands generally serves as a reliable index of graphitization degree of the carbon materials. (the smaller the ratio of I_D/I_G , the higher graphitization of the carbon).



Figure S5. (a) Cycling performance of various polyHIPE-carbon materials at a low current density of 100 mA g^{-1} ; (b) TGA curves of CF/Fe₃O₄-FS composites with different carbon contents.



Figure S6. Dependence of the specific capacities on the current densities for various CF/Fe₃O₄-FS composites.



Figure S7. Top view FESEM images of CF/Fe₃O₄-FS-2 after 50 cycles at the low (a) and high (b) magnifications; (c) EDS element maps of the (Figure S7b) CF/Fe₃O₄-FS-2 electrode after 50 cycles.



Figure S8. The post mortem FESEM examination of the CF/Fe₃O₄-FS-2 electrode and corresponding elemental maps of Fe, P, C, F and O.



Figure S9. XRD patterns of various carbon foam encapsulated FeS free-standing electrodes.



Figure S10. (a) the 1st, 2nd, 10th, 30th and 50th charge–discharge curves of a CF/FeS NR composite electrode; (b) cycling performance of various CF/FeS composite electrodes measured at a current density of 200 mA g⁻¹.

Figure S10a exhibits the discharge-charge curves of CF/FeS NR composite at 1^{st} , 2^{nd} , 10^{th} , 30^{th} and 50^{th} cycles. The first discharge curve exhibits the typical characteristic of a multiple discharge process: 1) The small plateau at 1.25 V (marked by circle I) corresponds to the reaction of FeS with Li⁺ forming Fe and Li₂FeS₂ (described by Equation as $2FeS+2Li^++2e^-=Li_2FeS_2+Fe(1)$. The subsequent plateau located at 0.8 V is related to the conversion reaction FeS+ $2Li^++2e^-=Li_2S+Fe$ (2). It is also worth noting that this plateau might partially be derived from the reduction of the

amorphous FeO_x to Fe since the surface atom at the nanosize FeS is readily oxidized. However, it is really difficult to distinguish the overlapped process in region II in our case. Process III of the long sloping discharge curve ranging from 0.8V to 0.1V associates with the formation of SEI layer, absorption of Li⁺ at the interfacial surface of nanosize particles as well as the Li⁺ intercalation into the carbon foam. During the 1st charge profile, voltage slopes can be observed at 1.8–2.0 V marked by circle IV, which is associated with the re-oxidation process of Fe to Li₂FeS₂. This large initial capacity loss of CF/FeS NR electrode is attributed to combined effect of the consumption of SEI layer and the irreversible reaction as indicated in reactions 1 and 2. From the 2^{nd} cycle onwards, the shoulder plateau regions located at ~ 1.3-1.4 V for discharge curves and at ~ 1.8 -1.9 V for charge curves agree well with the formation of Li₂FeS₂ and Li_{2-x}FeS₂, respectively, this reversible couple enables the application of FeS for Li⁺ storage.^[1] The CF/FeS NR free-standing electrode delivers an initial discharge capacity of 936 mA h g⁻¹ and a subsequent charge capacity of 596 mA h g⁻¹, leading to a relative low CE of 63.6%. The CE was increased to 93.2% during the 2nd cycle and stabilized higher than 98% after 5th cycle. Figure S10b demonstrates the cyclic performance of various CF/FeS composite electrodes. At a current density of 200 mA g⁻¹, the reversible capacity of 436 mA h g⁻¹ and 361 mA h g⁻¹ could be maintained after 50 cycles for CF/FeS NR and CF/FeS NS composites, respectively. The relative stable cyclability could be attributed to several factors: 1) the uniform in-situ growth of FeS on the supportive carbon substrate and 2) the complete carbon encapsulation of FeS which trap the intermediate product---polysulfides generated during the conversion reaction of sulfides, alleviating their dissolution in the organic solutions.^[1] In comparison, the CF/FeS NF composite with higher degree of aggregation of FeS nanosheet building blocks suffered from a more severe capacity decay from 541 mA h g⁻¹ to 340 mA h g⁻¹ upon 30 cycles, implying the crucial role of evenly spatial distribution of electroactive FeS on the carbon foam substrate for the stable cyclability.

[1] C. Xu, Y. Zeng, X. Rui, N. Xiao, J. Zhu, W. Zhang, J. Chen, W. Liu, H. Tan, H. H. Hng, Q. Yan, Controlled Soft-Template Synthesis of Ultrathin C@FeS Nanosheets with High-Li-Storage Performance. ACS Nano 2012, 6, 4713-4721.