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Supporting Information

Cobalt Sulfide Nanoflakes Grown on Graphite Foam for Na-Ion Batteries with Ultrahigh Initial Coulombic Efficiency

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Experimental Section

Material Preparation

1. Synthesis of GF

GF was prepared using a modified chemical vapor deposition based on a previously reported method.[1,2] In detail, some pieces of nickel foam were firstly immersed with 2 M HCl for 3 h to completely remove surface oxides and impurities. The clean nickel foam was then calcinated in a tube furnace at 1000 ℃ for 10 min under a mixed gas flow of CH_4 (150 sccm), H_2 (100 sccm) and Ar (800 sccm) to obtain graphite coated nickel foam. Finally, GF with an areal density of ~0.9 mg cm^{-2} was obtained by thoroughly etching nickel from the graphite coated nickel foam using $FeCl_3$/HCl (1 M/1 M) solution.

2. Synthesis of CoS_x NF@GF

Co_9S_8/CoS nanoflakes were grown on GF through a solvothermal route. In a typical synthesis, the solution was first prepared by dissolving 2.5 mmol of cobalt acetate tetrahydrate [$Co(CH_3COO)_2 \cdot 4H_2O$] and 2.5 mmol of thioacetamide in a mixed solvent (22 mL of H_2O/18 mL of ethanol), and then transferred into a 50 mL Teflon-lined autoclave containing a piece of GF (2.5×5 cm^2). The autoclave was sealed and maintained in an oven at 180 ℃ for 12 h. After being cooled to room temperature, the sample was rinsed with deionized water and ethanol three times, and subsequently dried at 80 ℃ in vacuum to obtain the final product marked as CoS_x NF@GF. The CoS_x loading was ~0.9 mg cm^{-2}.

3. Synthesis of CoS_x Film@GF

CoS_x Film@GF was prepared through a one-pot hydrothermal method. Typically, a piece of GF was immersed into a 40 mL of aqueous solution of 1.2 mmol of cobalt acetate tetrahydrate

[$Co(CH_3COO)_2 \cdot 4H_2O$] and 1.2 mmol of thioacetamide in an autoclave, and then kept at 180 ℃ for 12 h to obtain the sample CoS_x Film@GF.

Material Characterization

XRD (Bruker D8 Advance) was used to measure the crystalline structures of the samples. The morphologies and EDS elemental mappings of the samples were characterized by SEM (JEM-6700F). The chemical and electronic state of the elements within the samples were identified by XPS (VG ESCALAB 220i-XL). The microstructures of the samples were investigated by HRTEM (JEM-2010/UHR).

Cell Assembly

For all the electrochemical performance test, CR2032 coin half cells were assembled in an Ar-filled glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). For CoS_x NF@GF-based cells, a freestanding CoS_x NF@GF (a punched disk with a diameter of 10 mm) without any binder or additive was used as the working electrode, a disk of sodium foil was used as the counter electrode, as well as glass fiber (Whatman GF/D) was used as the separator. Two different electrolytes were used, one was 1 M $NaCF_3SO_3$ in diethylene glycol dimethyl ether (diglyme) and the other was 1 M $NaCF_3SO_3$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume). The assembling procedure of CoS_x Film@GF-based and GF-based cells was the same as that of CoS_x NF@GF. The mass loading of active materials was about 0.9-1.2 mg cm^{-2}.

Electrochemical Measurements

Galvanostatic discharge/charge measurements were performed using a Neware battery testing system in the voltage window of 0.4-2.9 V (vs. Na^+/Na) at different current densities. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using Solartron 1470E. CV measurements were conducted at a scanning rate of 0.1 mV

s^{-1} between 0.4 and 2.9 V. EIS tests were conducted in a frequency range from 100 kHz to 0.01 Hz with a signal amplitude of 5 mV.

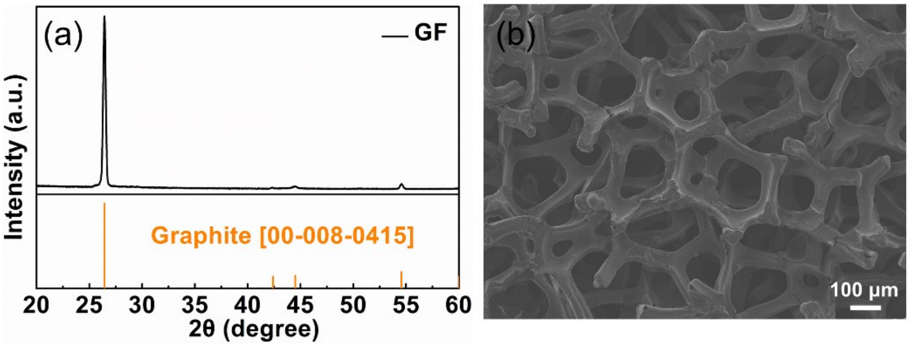

Figure S1. (a) XRD pattern and (b) SEM image of pure GF.

The XRD diffraction peaks (**Figure S1a**) can be assigned to graphitic carbon (JCPDS card no. 00-008-0415) without other impurity phases. In addition, the highly crystalline structure of GF was indicated by the strong and sharp XRD reflections, which suggests high conductivity of substrate GF that enhances electronic kinetics of cobalt sulfides. **Figure S1b** presents the SEM image of GF. The GF was revealed to be highly macroporous with interconnected network structure, which exhibits rather low areal density and excellent mechanical flexibility that offers sufficient buffer for the volume changes of cobalt sulfides.

Table S1. Initial capacity loss of the previously reported typical carbon materials in diglyme-based electrolytes for SIBs.

Carbon	Electrolyte	1st Discharge Capacity (mAh g^{-1})	ICE (%)	Initial Capacity Loss (mAh g^{-1})
rGO	1M $NaCF_3SO_3$ in Diglyme	~726	74.6	~184
CMK-3	1M $NaCF_3SO_3$ in Diglyme	~550	62.8	~205
Activated Carbon	1M $NaCF_3SO_3$ in Diglyme	~364	59.6	~147

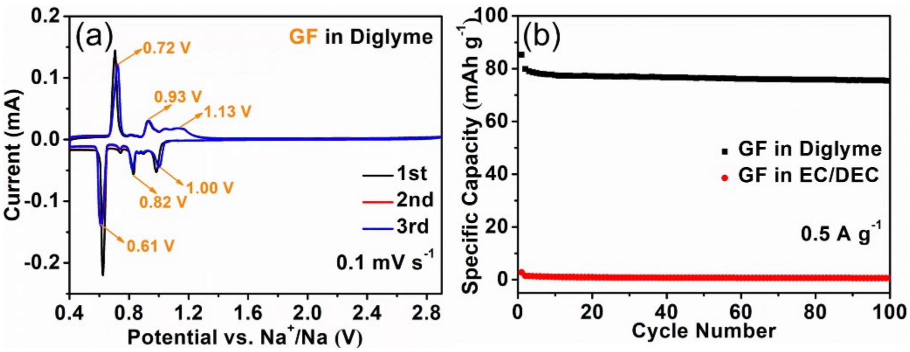

Figure S2. (a) CV curves of pure GF in diglyme-based electrolyte at a scan rate of 0.1 mV s^{-1}. (b) Cycling performance of GF in diglyme-based and EC/DEC-based electrolytes at 0.5 A g^{-1}.

To have a clue about the capacity contribution of GF substrate within the CoS_x NF@GF anode composite, the cycling performance of pure GF in diglyme-based and EC/DEC-based electrolytes was measured at 0.5 A g^{-1} (**Figure S2b**). The capacity contribution of GF in diglyme-based electrolyte was evaluated to be ~75 mAh g^{-1}, originating from the reversible intercalation reaction of solvated sodium ions by diglyme into GF. In contrast, the capacity contribution of GF in EC/DEC-based electrolyte was almost zero, as the formation of Na-rich binary graphite intercalation compounds is thermodynamically unfavorable.

References

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2. J. L. Liu, L. L. Zhang, H. B. Wu, J. Y. Lin, Z. X. Shen and X. W. Lou, *Energy Environ. Sci.*, 2014, **7**, 3709-3719.