Unveiling the Bimetallic FeCo Coupled MoS₂ Composite for Boosted Energy Storage

Qidi Yang^{a,c,1}, Yaoyao Xiao^{b,1}, Guohui Qin *^b, Jingying Duan ^{a,c}, Chengyang Wang *^{a,c}

^a School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

^b State Key Laboratory Base for Eco-Chemical Engineering, College of Chemical Engineering,

Qingdao University of Science and Technology, Qingdao 266042, Shandong, China. E-mail:

guohuiq163@sina.com

^cCollaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072,

PR China

¹ These authors contributed equally to this work and should be considered co-first authors.

Corresponding author.

E-mail address: guohuiq163@sina.com

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Table S1. The comparison fitted data of Rs, R_{SEI} , R_{CT} and R_b before and after 100cyclesat100mA g^{-1} forMoS₂basedsamples.

S1. Experimental section.

Preparing Prussian blue (PBA) cube. Firstly, 0.079 g cobalt chloride and 0.7058 g sodium citrate dispersed in 32 mL of H_2O (named solution A), 0.1974 g potassium ferricyanide was dissolved into 32 mL of H_2O (designated as solution B), afterwards solution A was slowly added into solution B and kept stirring for 24 h and the products were collected by centrifugation and washed with H_2O and ethanol for several times.

Synthesis of PBA@RF. The coating of resorcinol-formaldehyde Resin (RF) over PBA was performed. The above synthesized PBA particles were firstly modified by polyvinylpyrrolidone (PVP, molecular weight 8000) and dispersed in 29 mL of deionized water. 100 μ L of aqueous ammonia solution (25 wt%) and 0.03 g of resorcinol (dissolved in 1 mL of deionized water) were added into the above solution, and then 42 μ L of formaldehyde (37 wt %) was dropwise added, kept stirred for 3 h at 50°C. The obtained PBA@RF was collected by filter, washed with deionized water and ethanol for several times, dried in an oven at 100°C.

Synthesis of porous FeCo@C. PBA@RF was heated to 700°C under N₂ atmosphere and remained for 2 h. Finally, the porous FeCo@C was successfully prepared. The FeCo was obtained via the similar post annealing procedure of the PBA substrate.

Synthesis of FeCo@C@MoS₂. 45 mg of FeCo@C was dispersed into 50 mL of deionized water before adding 0.08 g of CTAB, kept stirred for 1 h, collected by centrifugation and cleaned with deionized water for 3 times and finally the products were dried in an oven at 100°C. The obtained products were dissolved in 30 ml deionized water followed by adding 0.05 g of ammonium molybdate tetrahydrate and 0.01 g thiourea. The obtained mixture was transferred to the reactor, sealed and reacted at 180°C for 12 h and got the product FeCo@C@MoS₂. The obtained FeCo@C@MoS₂ was washed with 0.5 M HCl at 90°C for 3 h, and got the C@MoS₂ sample. The MoS₂ was prepared via the similar procedure without the addition of FeCo@C sample, while the FeCo@MoS₂ was prepared via the FeCo structure instead of the FeCo@C.

Materials characterization. The morphology, structure and composition of the prepared materials were investigated via Hitachi S-4800 field emission scanning electron microscope (FESEM) and Hitachi JEM-2100F Transmission electron microscope (TEM). The X-ray diffraction (XRD) patterns were investigated by a Bruker D 8 Focus Powder X-ray diffractometer. The Raman scattering spectra was performed on a DXR Microscope Raman microscope with an excitation wavelength of 532 nm. The nitrogen adsorption desorption isotherms and pore size distribution curves were studied via ASAP- 2020M (BET). The X-ray photoelectron spectroscopy data was analyzed via a ESCALab220i-XL X-ray photoelectron spectrometer (XPS).

Electrochemical measurements. Electrochemical performance was investigated via

coin-type SIB/KIB cells (2032) assembled in an argon-filled glove box. The electrode consisted of active material, carbon black, and polymer binder (polyvinylidene difluoride, PVDF) in a weight ratio of 80:10:10. Next, certain amount of MoS₂ based materials were added into the mixture. The mixed slurry was casted the copper foil and dried at 120°C for 24 h under vacuum before being fabricated into coin cells. The loading of active materials in electrode is around 3mg. For sodium batteries, 1 M NaClO₄ dissolved in a mixture (1:1 in wt%) of ethylene carbonate (EC)dimethylcarbonate (DMC) was introduced as the electrolyte. The potassium battery electrolyte was a carbonate electrolyte (60 µL, 0.5 M KPF6 in propylene carbonate/ethylene carbonate (1:1). Galvanostatic charge/discharge tests were finished on a LAND CT2001A battery test system (0.01-3 V) at room temperature. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) data were finished via electrochemical workstation (CHI 660 D, CHI Company) in the frequency range of 0.1 Hz to 100 kHz. Electron paramagnetic resonance (EPR) test was finished via a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band). The symmetrical cell K-FeCo(a)C(a)MoS₂ | K-FeCo(a)C(a)MoS₂ was fabricated with vertically oriented K-FeCo@C@MoS₂-Cu- K-FeCo@C@MoS₂ array, in which the polypropylene film (Celgard 2500; USA) was used as the separator with a common carbonate electrolyte. The symmetrical cell K-FeCo(a)C(a)MoS₂ | K-FeCo(a)C(a)MoS₂ shows potassium stripping/plating behaviors based on such oriented K-FeCo@C@MoS2-Cu-K- $FeCo@C@MoS_2$ arrays. From the cycling performance in a symmetric cell at certain current density, we can obtain the voltage hysteresis and cell polarization information.

S2. Computational Method

For both crystal information prediction and geometry optimization, Density functional theory (DFT) calculations were rendered and performed in the Vienna Ab initio Simulation Package (VASP). A projector augmented-wave (PAW) technique based on spin-polarized PBE (Perdew, Burke, and Ernzerhof) exchange-correlation functional (a generalized gradient approximation) is introduced in these computations. Noticeably, for all calculations, total electronic and ionic relaxation energy is converged to 3×10^{-4} eV and 0.002 eV/Å, respectively, and the energy cutoff of 520 eV was used for plane wave basis set. The crystal geometry was built on the optimization of volume, the ionic positions, and cell shape. The partial occupancies were obtained via a tetrahedron method with Blochl calibrations. The most rational MoS2 structures were calculated according to probabilistic model. In this approach, Mo (4+) and S (2-) is continuously substituted via a large variety of configurations until ground state energy is achieved, however, retaining the crystal structure is the prerequisite. The most rational structures for MoS₂ unit cell is P2 1/m, Pnma and P2 1/c space group. Remarkbly, the experimentally determined crystal structures of MoS₂ (hexagonal) and elemental sulfur (orthorhombic) were further relaxed to calculate their formation energies by the PAW-PBE functionals. Significantly, obtained formation energies were rendered to evaluate the variation of MoS₂ based heterojunction. Considering the volume change of this solid state decomposition reaction can be not to predominately designated, the differentiated DFT-estimated energies can approach the kinetics and thermodynamics of the reactions.



Fig. S1 (a) The TGA curves of FeCo@C@MoS₂.XPS spectrum of FeCo@C@MoS₂ for (b) O and (c) N.

As shown in Figure S1(a), the TGA curve of FeCo@C@MoS₂ is mainly divided into tow parts in the temperature range of 80 to 1000 °C:

$$I .300 - 500^{\circ}C : MoS_2 + O_2 \rightarrow MoO_3 + SO_2$$

$$\tag{1}$$

$$2Co+O_2 \rightarrow CoO \tag{2}$$

$$3Fe+2O_2 \rightarrow Fe_3O_4$$
 (3)

$$C+O_2 \rightarrow CO_2 \tag{4}$$

II .680°C-850°C: The evaporation of MoO₃ in air

1. the MoS₂ content of FeCo@C@MoS₂ is estimated by

$$m (\text{FeCo}@C@MoS_2) = (n(MoO_3) \times M(MoS_2))/m_1(\text{wt.\%}) \times 100\text{wt.\%} = (m_2-m_3)(\text{wt.\%})/M(MoO_3) \times M(MoS_2)) / m_1(\text{wt.\%}) \times 100 \text{ wt.\%} = (71.4 / 144 \times 160) / 100) \times 100 \text{ wt.\%} = 79.3 \text{wt.\%}$$

2.the FeCo content of FeCo@C@MoS₂ is estimated by

$$m \operatorname{FeCo}(\operatorname{COMoS}_2) = (n(\operatorname{Fe}_3O_4/\operatorname{CoO}) \times M(\operatorname{FeCo}))/m_1(\operatorname{wt.\%}) \times 100 \operatorname{wt.\%} =$$

 $m_3(wt.\%)/M(Fe_3O_4/CoO) \times M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / m_1(wt.\%) \times 100 wt.\% = (18.9/114.3 \times 57.5) / M(FeCo)) / M(FeCo)) / M(FeCo) = (18.9/114.3 \times 57.5) / M(FeCo)) / M(FeC$

 $100) \times 100$ wt.% = 9.5wt.%

3. the CN content of FeCo@C@MoS₂ is estimated by

m(FeCo@C@MoS₂) =100 wt.%-79.3 wt.%-9.5 wt.%=11.2wt.%



Fig. S2 (a) N_2 adsorption and desorption isotherm and (b) pore size distribution of MoS₂ based composites. (c) The TEM image of MoS₂. (d) The TEM image of FeCo@MoS₂.



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Table S1 The comparison fitted data of Rs, R_{SEI} , R_{CT} and R_b before and after 100 cycles at 100 mA g^{-1} for MoS_2 based samples

	Sample	$R_S\!/\Omega$	$R_{SEI}\!/\!\Omega$	R_{CT}/Ω	R_b/Ω
New battery	Pure MoS ₂	2.643	544.4	19.71	320
	$C@MoS_2$	4.004	93.21	1.742	15.17
	FeCo@C@MoS ₂	3.698	106.6	1.05	106.3