Supporting Information

Boosting Catalytic Activity by Interfacial Electric Field of VN-V₂O₃ Heterogeneous Nanoparticles for Efficient Lithium Polysulfide Conversion

Yuxin Fan[†], Yongzheng Zhu[†], Zheng Wei, Huibing He, Jinliang Zhu*

School of Resources, Environment and Materials, Guangxi Key Laboratory of Processing for Non-ferrous Metals and Featured Materials, Guangxi Key Laboratory of Processing for Non-ferrous Metals and Featured Materials, Guangxi University, Nanning 530004, P. R. China.

[†]*These authors contribute equally to this work E-mail: jlzhu85@163.com; jlzhu@gxu.edu.cn*

Experimental section

Synthesis of VN-V₂O₃/C, VN /C and V₂O₃/C

50 g of the resin powder (Tianjin Resin Technology Co., Ltd., China) was added to 300 ml of vanadium chloride (0.0225 mol; Shanghai Aladdin Biochemical Technology Co., Ltd) solution and then agitated under 50 °C at a constant speed for 5 hours. Subsequently, the existing mixture was filtered and the gathered resin was desiccated at 80 °C for 24 hours. The V³⁺-containing resin was obtained after filtration and drying. Then, V^{3+} -containing resin was milled with potassium hydroxide (1:0.3) for 10 minutes. Whereafter, the mixture which was adequately ground was pyrolyzed in the tube furnace at 850 °C in nitrogen atmosphere for 1 hour, and the heating rate is 5 °C min⁻¹. When cooling completely to room temperature, the product was immersed in deionized water and scrubbed with deionized water several times until the pH value of the filtrate approached 7. Then the filter paper was dried at 70 °C for 12 hours to obtain VN- V_2O_3/C . VN/C is synthesized via the same method except the ratio of V³⁺-containing resin to KOH is 1:0.4 at 900 °C. Furthermore, V₂O₃/C obtained via cooling in mixed gas ($V_{Nitrogen}/V_{Oxvgen} = 95:5$). Inductively coupled plasma-atomic emission spectrometry (ICP) analysis exhibited that the VN-V₂O₃/C, VN/C, and V₂O₃/C contents within the prepared samples were 31.7, 29.5 and 30.8 wt%, respectively.

Synthesis of VN-V₂O₃/C@S

 $VN-V_2O_3/C$ and sulfur powder (99.98 wt%, Sigma-Aldrich) were mixed in a mass ratio of 1:3 and subjected to ball milling for 30 minutes. The resulting mixture was then

transferred to a hydrothermal reactor lined with Teflon, heated to 155°C, and allowed to react for 12 hours.

Physical characterization

XRD patterns were obtained using a D/Max-III X-ray diffractometer (Rigaku Co., Japan) with Cu Ka radiation, operating at a voltage of 40 kV and a current of 30 mA. The Raman spectroscopy was performed on a Raman spectrometer with a 532 nm He/Ne laser (Horiba Jobin Yvon Inc, France). The specific surface area and pore size distribution were analyzed using an ASAP 2460 surface area analyzer (Micromeritics Co., USA). The sulfur content was analyzed using a thermogravimetric analyser (DSC/TGA; Netzsch STA449 F5 Jupiter), with the TGA test conducted from 30 to 850°C at a heating rate of 5°C min⁻¹ under N₂ atmosphere. UV-vis adsorption spectra were measured by an ultraviolet/visible spectrophotometer (PerkinElmer Lambda650, USA). The surface state and chemical environment of the samples were analyzed by monochrome Al Ka radiation photoelectron spectroscopy (XPS, ESCALab 250Xi, ThermoFisher Scientific, USA; Al Ka). The microstructural analysis and elemental distribution of the materials were investigated using a field-emission scanning electron microscope (SEM, SU8820, Hitachi Co., Japan) and a transmission electron microscope (TEM, Titan ETEM G2, USA).

Visualized adsorption tests and the corresponding UV-vis spectra

A mixture of sulfur and Li_2S (mole ratio: 1:5) was added to a solution of 1,2dimethoxyethane/1,3-dioxolane (DME/DOL, 1:1 v/v) and stirred at 60°C for 24 hours to obtain a Li_2S_6 solution. Subsequently, 20 mg of host materials were added to 4 mL Li_2S_6 solution, and photographs were taken after 3 hours. The adsorption properties of the three host materials were then evaluated using UV-vis spectrophotometry.

Symmetric cells test

To prepare the electrodes for the symmetrical cells, WC-WO₃/C, WC/C, and WO₃/C were thoroughly mixed with polyvinylidene fluoride (PVDF) at a mass ratio of 9:1 in N-methyl pyrrolidone (NMP), forming a homogeneous slurry. The slurry was uniformly coated onto a carbon cloth (diameter: 14 mm) and subsequently dried at 60°C for 12 hours. The loading of the host materials on the carbon cloth is 1.0 mg cm⁻². Two identical carbon clothes were then assembled into a CR2032-type coin cell, using 0.2 mol L⁻¹ Li₂S₆ solution (1:1 v/v DME/DOL solution containing 1.0 M LiTFSI and 1 wt% LiNO₃ as the electrolyte. Cyclic voltammetry (CV) curves were obtained at a sweep rate of 1 mV s⁻¹ over a voltage range of -1.0 to 1.0 V.

Li₂S nucleation tests

The precipitation and dissolution test cells utilized the same cathodes as the symmetric cells, with the only difference being the use of lithium metal as the anode. A Li_2S_8 solution (0.20 mol L⁻¹) was prepared by mixing sulfur and Li_2S at a molar ratio of 7:1 in 1:1 DME/DOL (v/v) solution containing 1.0 M LiTFSI and 1 wt% LiNO₃. The mixture was vigorously mixed at 60°C for 24 hours. A consistent amount of 20 μ L

 Li_2S_8 solution was added to the cathode side and then 20 µL electrolyte (1:1 v/v DME/DOL solution containing 1.0 M LiTFSI) was in the anode side. In the Li_2S precipitation test, the prepared cells were galvanostatically discharged to 2.06 V under 0.112 mA, followed by potentiostatically discharged at 2.05 V.

Electrocatalytic activity evaluation

The electrocatalytic activity evaluation was conducted using a three-electrode system at an electrochemical work station (Pine Instrument Co., USA). The working electrode consisted of a rotating disk electrode (RDE) with a glassy carbon electrode, while lithium foil served as both the counter and reference electrodes. A dispersion of 5 mg of electrocatalyst in the mixture of 483 μ L isopropanol, 483 μ L deionized water, and 33 μ L of Nafion (0.5 wt%, DuPont, USA) was prepared. The resultant mixture was ultrasonicated for 30 minutes, and then 4 μ L suspension was uniformly loaded on the electrode using the drop-casting method. The areal loading of the electrocatalyst on the working electrode was set to be 0.1 mg cm⁻². All the electrocatalytic properties were characterized in electrolytes comprising 4.0 mM S₈ and 1.0 M LiTFSI dissolved in DME/DOL (1:1 v/v). The electrocatalytic activity on S₈ reduction reaction was investigated using linear scanning voltammetry (LSV) in the voltage range of 3.0-1.5 V vs Li⁺/Li, with a scan rate of 10 mV s⁻¹ at 1000 rpm. The corresponding Tafel slopes were calculated from the Tafel equation based on the LSV curves.

Electrochemical measurements

The electrode slurry was prepared by combining composite materials (WC-WO₃/C@S, WC/C@S, and WO₃/C@S) with Super P and PVDF in a mass ratio of 8:1:1

in NMP solution. The slurry was then coated onto aluminium foil and dried at 55°C for 12 hours. The aluminium foil coated with the active material was cut into round pole pieces with an areal sulfur loading of 1.7 mg cm⁻² as the working electrodes. These electrodes were used as the cathodes of Li-S batteries, and a lithium metal sheet as the anode. The electrolyte for the Li-S batteries consisted of 1.0 M LiTFSI with 2 wt% LiNO₃ in a DOL/DME (1:1, v/v) solution, with each cell being injected with 30 μ L of electrolyte. The batteries were assembled using a coin cell (CR 2032) in an Ar filled glove box (H₂O < 0.1 ppm, O₂ < 0.1 ppm). The electrochemical performances were estimated using a battery testing system (Shenzhen Neware Battery Co., China) within a voltage range of 1.7-2.8 V at room temperature (about 25°C). The CV curves were measured using an IM6 electrochemical workstation (Zahner-Elektrik, Germany) within a potential range of 1.7-2.8 V, and electrochemical impedance spectroscopy (EIS) was conducted with a frequency range of 10⁻¹ to 10⁵ using a voltage amplitude of 5 mV.

Li-S pouch cell assembly

The electrode slurry composition was prepared using the same method as the coin cell. The slurry was coated on carbon-coated aluminium foil and the sulfur loading is approximately 7.0 mg cm⁻². After drying at 60°C for 12 hours, the coated aluminium foil was cut into 4.5 cm \times 5.5 cm shape to be used as the cathode. Anodes were made using lithium sheets (50 µm), and Celgard 2400 PP membranes were utilized as separators. The cathodes and anodes were layered and stacked using a laminating machine, and initial encapsulation was achieved through side sealing technology. The

electrolyte for the Li-S pouch cell consisted of 1.0 M LiTFSI with 2 wt % LiNO₃ in a DOL/DME (1:1, v/v) solvent. The amount of electrolyte was carefully controlled to achieve an E/S ratio of $3.0 \,\mu$ L mg⁻¹. Following a 12-hour standing period, the assembled pouch cell was tested within the same voltage range as the coin cell. The energy density was calculated using the following equation:

$$E = E_d / \sum (m_{areal})_i \tag{1-1}$$

Where *E* is the gravimetric energy density, E_d is the discharge energy at the first cycle, m_{areal} is the areal mass loading of the cell components. The total mass of Li-S pouch cell is 3.79 g, where contains the mass of VN-V₂O₃/C cathode, electrolyte, and other materials (Li anode, Al current collector, separator, and tap). The specific calculation process for the energy density of the first cycle is as follows:

$$E_g = \frac{2.1 \times 633.7}{3.79} = 351.1 \, (Wh \, kg^{-1}) \tag{1-2}$$

Density functional theory (DFT) calculations

DFT calculations were performed within Vienna Ab initio Simulation Package (VASP) based on the density functional theory (DFT). The generalized gradient approximation (GGA) calculation was carried out within the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential. The DFT+D3 with Becke-Johnson damping was applied to describe the vander Waals interaction between layers. The plane-wave cut-off energy was set to 500 eV for geometry optimization. A $3 \times 3 \times 1$ Monkhorst-Pack grid was used for sampling the Brillouin zones at structure optimization. The convergence criteria of structure optimization was chosen as the maximum force on

each atom less than 0.01 eV Å⁻¹ with an energy change less than 10⁻⁵ eV. The binding energy was calculated as follows:

$$E_{ads} = E_{total} - E_{sub} - E_{LiPSs} \tag{1-3}$$

where E_{total} is the total energy of the LiPSs adsorbed systems, E_{sub} and E_{LiPSs} are the energy of the substrate and the isolated LiPSs molecule, respectively.



Fig. S1. SEM, TEM, and HRTEM images of (a-c) VN/C, (d-f) V₂O₃/C.



Fig. S2. (a-c) N_2 adsorption/desorption isotherm and (d-f) pore size distributions of $VN-V_2O_3/C$, VN/C, and V_2O_3/C .



Fig. S3. (a) XPS survey of VN-V₂O₃/C. The high-resolution XPS spectra of (b) O 1s and (c) N 1s.



Fig. S4. TGA curves of $VN-V_2O_3/C@S$.



Fig. S5. V 2p XPS spectra of VN-V₂O₃/C after Li_2S_6 adsorption.



Fig. S6. CV curves of (a) VN-V₂O₃/C@S, (b) VN/C@S, (c) V₂O₃/C@S. (d) Arrhenius

plots of the three cathodes.



Fig. S7. GITT voltage profiles of VN/C@S and $V_2O_3/C@S$.



Fig. S8. Adsorption configurations and adsorption energies of S_8 , Li_2S_6 , Li_2S_4 , and Li_2S on the (a) VN-V₂O₃, (b) V₂O₃, and (c) VN surfaces.



Fig. S9. UPS spectra of (a) VN-V₂O₃/C, (b) VN/C, and (c) V₂O₃/C.



Fig. S10. Cycling performance of the pouch cell using VN-V₂O₃/C@S cathode at 0.05

C.