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Highly Activity and Stable Oxygen Vacancies by Sulfur Modifying for Efficient

Catalysis in Lithium-Sulfur Batteries

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1. Experimental Procedures

1.1 Synthesis of BOC/rGO, and reduced graphene oxide

A method of modified Hummer was used to synthesize Graphene oxide 4 from crystalline flake graphite. 30 mL of 2 mg/mL graphene oxide solution were prepared and 13 mg of ascorbic acid were infunded under stirring at 95 °C for 1 hour. Deionized water was used to wash the above solution for six times to obtain reduced graphene oxide (rGO) solution. In a typical synthesis of 50.0 mL glycerol were prepared to dissolve PVP (0.8 g) and Bi (NO₃)₃ (0.5 g) under continuous magnetic stirring for 1 hour until a milky white solution is obtained. 30mL of 2mg/mL rGO solution was slowly poured into the above solution under continuous magnetic stirring. A black solution was obtained after 1 hour of continuous stirring. 2.5 g of NaCl was dissolved in 10 mL of deionized water, which was slowly poured into the above black solution with continuous magnetic stirring for 30 minutes. Then, the prepared solution was reacted hydrothermally at 160 °C for 6 h. The resulting mixture was washed three times with ethanol and water, respectively. Finally, the obtained products were freeze dried for two days to obtain the BOC/rGO.

1.2 Synthesis of Vo-BOC/rGO, S-Vo-BOC/rGO

30 mg of the BOC/rGO powder prepared in the previous step was spread evenly on the bottom of a porcelain boat, and place it in a quartz tube. The BOC/rGO powder was heated at 200 °C for 2.0 h with 5 °C min⁻¹ in a 5% H₂/Ar atmosphere, and cooled down to room temperature naturally to obtain the Vo-BOC/rGO powder. To synthesize S-Vo-BOC/rGO, 30mg of Vo-BOC/rGO and 30 mg of S powder were placed on both sides of the same porcelain boat, and place it in a quartz tube. The S powder was located upstream of the airflow. The sample was heated at 200 °C for 2.0 h with a 5 °C min⁻¹ in Ar, and cooled down to room temperature naturally. The obtained sample was poured into CS₂ with continuous magnetic stirring for 1 hour. The resulting mixture was washed three times with ethanol and water, respectively. Finally, the obtained products were freeze dried for two days to obtain the S-Vo-BOC/rGO. Other steps remain unchanged, and the catalysts with different sulfur content can be obtained by controlling the quality of S during heating.

1.3 Preparation of Vo-BOC/rGO and S-Vo-BOC/rGO separators

Firstly, 4mg of the Vo-BOC/rGO and S-Vo-BOC/rGO powders obtained in the above experiments were placed in two glass bottles, respectively. Subsequently, 8.89 mg of a 5 *wt.*% PVDF solution dissolved in N-methylpyrrolidone (NMP) and 12 mg of NMP were added to the above glass bottles containing the powders. Then, the above glass bottles were put into an ultrasonic machine for ultrasonic mixing. The PVDF and the powders were adhered together uniformly during this process. Finally, the dispersed mixture was coated onto the Celgard polypropylene (PP) separators separately by vacuum filtration, and then dried at 60°C for 12h to obtain the separators coated with Vo-BOC/rGO and S-Vo-BOC/rGO.

1.4 Assembly and electrochemical measurements of Li₂S₆ symmetric cells

S and Li₂S with a ratio of 5:1were placed in a solution of DOL/DME (V_{DOL}/V_{DME}=1:1) with 1mol/L LiTFSI and 0.2mol/L LiNO₃, and stirred at 40 °C until completely dissolved to obtain Li₂S₆ solution. The Vo-BOC/rGO and S-Vo-BOC/rGO powders, and PVDF binder (5 *wt*.% with NMP) were

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mixed in a mixer at a ratio of 9:1 with appropriate amount of NMP to obtain a uniform slurry. Whereafter, the prepared slurry was spread evenly on the aluminum foil current collector using a mold and dried at room temperature for 12 h, and a disk with a diameter of 12 mm was punched in it. Cyclic voltammetry measures were performed at the scan rate of 2 mV s⁻¹ between 1V and -1V.

1.5 Experiments on Li₂S nucleation and decomposition

Similar to the preparation method of Li₂S₆, S and Li₂S with a ratio of 7:1were placed in a mixed solution of DOL/DME (V_{DOL}/V_{DME}=1:1) with 1mol/L LiTFSI and 0.2mol/L LiNO₃ and stirred at 40 °C until completely dissolved to obtain Li₂S₈ solution. The Celgard 2400 separator was sandwiched between Vo-BOC/rGO or S-Vo-BOC/rGO sulfur-free cathode and lithium metal anode, and Li₂S₈ solution was added as the electrolyte to assemble batteries for experiments on Li₂S nucleation and decomposition. For the Li₂S nucleation experiment, the battery obtained above was discharged galvanostatically to 2.13V under 0.1mA, and then discharged potentiostatically at 2.05 V until the discharge current dropped to 10⁻⁵ A to collect the full charge and evaluate the Li₂S nucleation/growth rate. For the Li₂S decomposition experiment, the battery was discharged galvanostatically to 1.8 V under 0.1 mA, and then discharged galvanostatically to 1.7 V under 0.01 mA to ensure completely conversion to Li₂S. After complete conversion, potentiostatically charging was performed at a voltage of 2.4 V until the charging current was below 10⁻⁵A to achieve complete decomposition of Li₂S.

1.6 Assembly and electrochemical measurements of lithium-sulfur batteries

Ketjen black carbon and sulfur powder were mixed (C:S = 7:3) by grounding for about 1 hour in a mortar, and then the mixed powder was placed in a Teflon-lined autoclave for 12 hours at 155°C followed with melting-diffusion. The autoclave cooled down to room temperature naturally to obtain a carbon-sulfur composite with a sulfur content of 70 wt.% The carbon-sulfur composite and LA133 binder (5 wt.% with water) were mixed in a mixer with a ratio of 9:1 with appropriate amount of water as a solvent to obtain a uniform slurry. Whereafter, the prepared slurry was spread evenly on the carbon-coated aluminum foil current collector using a mold and dried at room temperature for 12 h, and a disk with a diameter of 12 mm was punched in it to obtain cathodes. The carbon-sulfur electrode as cathode, lithium metal as anode, PP separator coated with functional materials, and 30 µL of electrolyte were assembled to obtain standard 2025 button lithium-sulfur batteries. The electrolyte was composed of 1 mol L⁻¹ lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and 0.2mol/L LiNO₃ dissolved in a mixed solvent of 1, 3-dioxolane (DOL) and dimethoxymethane (DME) (V_{DOL}/V_{DME}=1:1). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on an electrochemical workstation (ChenHua CHI650D). The lower and upper voltage limits for cyclic voltammetry were 1.7 V and 2.8 V respectively, and the frequency range for electrochemical impedance spectroscopy was 1 MHz to 0.1 MHz with an amplitude of 5 mV. The charge/discharge tests and cycling tests were measured from 1.7 V to 2.8 V by using a test system of batteries (Neware).

1.7 Material characterization

X-ray diffractometer with Cu Kα radiation (XRD, PANalytical X'Pert PRO, 40 mA, 40 kV) was used to characterize the crystalline structure of the prepared materials. Surface elements were analyzed by X-ray photoelectron spectroscopy measurements (XPS, Thermo Scientific). The morphology was characterized by transmission electron microscopy (TEM, FEI Tecnai G2 F30) and scanning electron microscopy (SEM, Hitachi SU8010). The contents of each substance in the composites were measured via a thermogravimetric analyzer system (Linseis STA PT 1600). The ultraviolet-visible (UV-vis) spectrum analysis was characterized via a Shimadzu UV-2450 Spectrophotometer. The Brunauer-Emmett-Teller method (BET, ASAP 2020, Micromeritics) was used to characterize the specific surface areas of the prepared materials.

1.8 Theoretical calculations

All ab initio calculations of this manuscript were carried out using the Quantum ESPRESSO package by a method of the density-functional theory (DFT), and the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) formulation was used. The ultrasoft pseudopotentials were chosen to describe the core electrons. The dispersion corrections were introduced by a method of DFT-D3. The energy cutoff of electronic wave functions and the charge density were set to 35 and 280 Ry, respectively. The BiOCI (101) surface was modeled using a (3×3) supercell slab and a 15 Å vacuum layer was modeled on the slab. The Brillouin zone with a 3 × 3 × 1 k-point grid was sampled. The convergence thresholds of total energy and force threshold were set to 10⁻⁶ Ry and of 10⁻³ Ry/Bohr for structural optimization, respectively. $\Delta E = E_{slab+ads} - (E_{slab} + E_{ads})$ was used for calculating the binding energy between substrate and adsorbed sulfur species. Among

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them, $E_{slab+ads}$ is the total energy of all absorbed system, E_{ads} represents the energy of the absorbed sulfur species and E_{slab} represents the energy of the slab after absorbing. $\sigma = \sigma^{unrel} + E^{rel}$ and $\sigma^{unrel} = 1/2(E_{surf} - N_{atoms} \cdot E_{bulk})$ are used for calculating the surface energies. Among them, σ is the surface energy, E^{rel} represents the relaxation energy of the slab, E_{bulk} represents the energy of single atom in bulk, E_{suf} represents the energy of the freshly cut slab, N_{atoms} is the number of the atoms in slab. $E_{Vo} = E_{defect} - E_{perfect} + 1/2\mu_{O2}$ is used for calculating the formation energies of oxygen vacancies. Among them, E_{Vo} represents the formation energies of oxygen vacancies, E_{defect} represents the energy of slab without oxygen vacancies and μ_{O2} is the chemical potential of O_2 . $\Delta G = \Delta E + \Delta ZPE$ - T ΔS was used for calculating Gibbs free energy change (ΔG) of each SRRs step. Among them, ΔE is the total energy difference, ΔZPE represents the change of zero-point energy, T was set as 298.15 K and ΔS is the change of entropy, respectively. The SRR steps are described by the equations (S1- S5). The climbing image nudged elastic band (CI-NEB) method was used to simulate Li₂S decomposition possess ($Li_2S \rightarrow Li^+ + e^- + LiS$).

$S_8^* + 2Li^+ + 2e^- \to Li_2S_8^*$	(S1)
$Li_2S_8^* + 2Li^+ + 2e^- \rightarrow Li_2S_6^* + Li_2S_2$	(S2)
$Li_2S_6^* + 2Li^+ + 2e^- \rightarrow Li_2S_4^* + Li_2S_2$	(S3)
$Li_2S_4^* + 2Li^+ + 2e^- \rightarrow Li_2S_2^* + Li_2S_2$	(S4)
$Li_2S_2^{\ *} + 3Li_2S_2 + 8Li^+ + 8e^- \to Li_2S^* + 7Li_2S$	(S5)

The asterisk (*) is the adsorbed state of the intermediates of SRRs

2. Supporting Figures and Tables



Figure S1. Optimized geometries of (a) BOC, (b) Vo-BOC, (c) S-Vo-BOC, (d) P-Vo-BOC (e) N-Vo-BOC



Figure S2. Optimized geometries after the adsorption of Li_2S_4 of (a) BOC, (b) Vo-BOC, (c) S-Vo-BOC, (d) P-Vo-BOC (e) N-Vo-BOC



Figure S3. Formation energy of oxygen vacancies for S-Vo-BOC and Vo-BOC

1µm



Figure S4. SEM images of (a) Vo-BOC/rGO and (b) S-Vo-BOC/rGO



Figure S5 S 2s high-resolution XPS spectrum of (a) S-Vo-BOC/rGO and (b) Vo-BOC/rGO



Figure S6. (a) High-resolution TEM image and (b) Brightness profile of HRTEM of BOC/rGO (101)



Figure S7. (a) High-resolution TEM image and (b) Brightness profile of HRTEM of S-Vo-BOC/rGO (101)



Figure S8. (a) High-resolution TEM image and (b) Brightness profile of HRTEM of Vo-BOC/rGO (002), (c) High-resolution TEM image and (d) Brightness profile of HRTEM of S-Vo-BOC/rGO (002).



Figure S9. Optimized slab geometries of (a) BOC, (b) Vo-BOC, (c) S-Vo-BOC



Figure S10. (a) TGA curve and (b) N_2 adsorption-desorption isotherms of S-Vo-BOC/rGO



Figure S11. O/CI ratio of EELS spectra and corresponding three regions



Figure S12. Differential charge diagram of Vo-BOC after S modifying.



Figure S13. UV-vis spectrums and corresponding optical photograph of a bare Li₂S_x solution and the Li₂S_x solutions with Vo-BOC/rGO and S-Vo-BOC/rGO after statical adsorption for 10 h.

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Figure S14. TGA curve of carbon-sulfur composite



Figure S15. Digital photos of (a) bare PP separator, (b) S-Vo-BOC/rGO@PP separator and (c) S-Vo-BOC/rGO@PP separator after bending. (d) Cross-section SEM image of the S-Vo-BOC/rGO@PP separator.



Figure S16. Contact angles between electrolyte and (a) commercial PP and (b)S-Vo-BOC/rGO modified separator.

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Figure S17. Tafel plots of cells with of Vo-BOC/rGO and S-Vo-BOC/rGO.



Figure S18. Potentiostatic charge profile of Li₂S dissolution on Vo-BOC/rGO and S-Vo-BOC/rGO





- Re: The internal resistance of the electrolyte;
- $R_{ct}\!\!:$ The charge-transfer resistance, related to the electrode reaction kinetics;
- Q: Capacitance of the electrode bulk in high-frequency region considering the dispersion effect;
- W: The semi-infinite Warburg diffusion impedance.



Figure S20. CV curves of the cell with (a)Vo-BOC/rGO and (b) S-Vo-BOC/rGO at various scan rates.

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Figure S21. Peak current density of (a) A1, (b) C1 and (c) C2 for cells with Vo-BOC/rGO and S-Vo-BOC/rGO vs. the square root of the scan rates.





Figure S22. Li₂S decomposition pathways on (a) Vo-BOC and (b) S-Vo-BOC.



Figure S23. Optimized geometries of Li_2S adsorbed on (a) Vo-BOC and (b) S-Vo-BOC.



Figure S24. Comparison of discharge capacity at different voltage plateau



Figure S25. discharge voltage profiles after magnification of S-Vo-BOC/rGO and Vo-BOC/rGO based cells under 0.2C.

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Figure S26. Galvanostatic charge-discharge profile of S-Vo-BOC/rGO cell with high sulfur loading under 0.2 C



Figure S27. cycling performance of S-Vo-BOC/rGO cell with high sulfur loading under 0.2 C