Organosulfur compounds, like other organic molecules (e.g., carbonyl compounds and organic radicals), have shown great potential as promising active materials for next-generation electrochemical energy storage (1–3). Among them, organodisulfides (RSSR; R is an organic group) are the simplest molecules, with high structural diversity. The redox reactions of RSSR are based on the reversible S-S bond breakage/formation (Fig. 1A). The first study by Visco et al. (4) for RSSR in energy storage applications dates back to the 1980s, using tetramethylthiuram disulfide as a cathode material for sodium batteries. Subsequently, Liu et al. (5) found that the reaction kinetics of various RSSR are sluggish, resulting from the large bond breakage energy required in the electrochemical reduction process, showing high overpotential and low energy efficiency (EE; ca. <80%). Recently, organosulfur as an electrode material has been attracting more attention, along with advances in lithium-sulfur batteries (6–10). Strategies to improve the sluggish kinetics of RSSR include the formation of organopolysulfide (R-Sn-R, n ≥ 3), usage of the N-heterocycle group, and selenium doping (Fig. 1B, 1–3) (11–13).

Redox flow batteries (RFBs) have become one of the most promising candidates for the storage of intermittent renewable energies (e.g., solar and wind) (14–16). In the flowable anolyte and catholyte, electroactive materials play a critical role in determining energy and power densities of the battery. Over the past 10 y, most of the work on RFBs has focused on material screening and optimization (17, 18). RSSR molecules are highly soluble in organic solvents, which makes them suitable as active materials in catholytes for RFBs (19–22). To improve the achievable capacity and reaction kinetics of RSSR, Weng et al. (23) reported an asymmetric allyl-activation strategy (R-Sn-A, n ≥ 2; Fig. 1B, 4), since the S-A bond can break in the discharge; therefore, it can obtain one more electron than RSSR. However, the insoluble Li2S generated in this process is not flammable, posing a serious challenge. Therefore, the pursuit of reliable chemical strategies to accelerate the sluggish kinetics of RSSR is of great significance.

Our aim here is to regulate and enhance the reaction kinetics of RSSR based on the reversible formation/breakage of the C-S bond involving carbon disulfide (CS₂) as a redox mediator (Fig. 1C). In the discharge, the negatively charged RSSR⁻ can interact with CS₂, forming RSCS₂Li as the discharged product, which reduces the energy barrier for the S-S bond breakage, promoting RSSR toward fast reaction kinetics. In the recharge, the C-S bond breaks, and CS₂ is unbonded from RSCS₂Li, forming RSSR as the recharged product. Meanwhile, CS₂ can also be inserted into the molecular structure of RSSR to form RSCS₂SR/RSCS₂CS₂SR, and these molecules can further accelerate the reaction kinetics of the redox reactions. Therefore, the EE in the cycle is significantly increased to over 90%. Phenyl disulfide (PhSSPh) as a simple aryl disulfide molecule has high solubility in the ether electrolyte (>3.0 M; SI Appendix, Fig. S1) and a high theoretical volumetric efficiency (EE; ca. 90%).

Significance

The intrinsic sluggish kinetics of organodisulfides has hindered its further application in large-scale energy storage. In this work, we propose a unique redox mediator (carbon disulfide [CS₂]) involving reversible C-S bond formation/breakage, which accelerates the reaction kinetics of organodisulfides by reducing about one-third of the energy barrier of sulfur–sulfur bond breakage. The strategy described here supplies a perspective for enhancing the electrochemical behavior of organodisulfides and greatly facilitates the development of organodisulfides in large-scale energy storage applications.
capacity (>160.7 Ah L\(^{-1}\); SI Appendix, Fig. S1), which makes it very promising in RFBs compared with other organic materials (SI Appendix, Fig. S2). It was first selected to demonstrate the feasibility of our strategy. PhSSPh with/without CS\(_2\) was dissolved in ether electrolyte as catholytes and lithium metal as a static anode to assemble a nonaqueous RFB (Fig. 2A), and their electrochemical behaviors were examined through a static and flow cell, which is considered an effective way to screen the initial materials for RFBs, especially in nonaqueous RFBs (24–26).

**Results**

As presented in Fig. 2B, PhSSPh shows a high potential difference of 0.39 V and a low achievable volumetric capacity of 15.4 Ah L\(^{-1}\), resulting from its intrinsic sluggish kinetics. After the CS\(_2\) is introduced to the PhSSPh-based catholyte, the potential difference in PhSSPh is significantly reduced to 0.10 V, and a high volumetric capacity of 19.5 Ah L\(^{-1}\) is achieved. The cell of PhSSPh/CS\(_2\) shows an ultra-high cycling stability (Fig. 2C), that

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**Fig. 1.** Background and research development. (A) Reversible reaction mechanism of RSSR. (B) Strategies for improving the reaction kinetics of RSSR. (C) Schematic illustration of CS\(_2\) as a redox mediator to regulate the electrochemical performance of PhSSPh.

**Fig. 2.** Battery performance. (A) Schematic diagram of a lithium RFB with PhSSPh/CS\(_2\) as the catholyte. (B) Galvanostatic discharge/charge curves of PhSSPh and PhSSPh/CS\(_2\) at 0.2 mA cm\(^{-2}\). (C) Capacity retention and EE of PhSSPh and PhSSPh/CS\(_2\) at 0.2 mA cm\(^{-2}\). (D) Rate performance of PhSSPh and PhSSPh/CS\(_2\). (E) A lithium flow cell. (F) Cycling performance of PhSSPh and PhSSPh/CS\(_2\) at 1.0 mA cm\(^{-2}\) in the flow cell. (The concentration of PhSSPh in the electrolyte is 0.5 M, and the molar ratio of PhSSPh:CS\(_2\) is 1:2).
is, 500 cycles (1,498 h) with a capacity fading rate of 0.039% per cycle and a high EE (>90%), which are all far better than PhSSPh alone (e.g., a high capacity fade of 0.133% per cycle [500 cycles, 928 h] with a low EE [<80%]); this indicates that the addition of CS₂ greatly improves the reversibility of PhSSPh and promotes maintenance of a high material utilization rate by PhSSPh during the cycling process, thereby improving its cycle stability. A high-concentration catholyte (2.0 M PhSSPh/4.0 M CS₂) was also assessed (SI Appendix, Fig. S3); the cell can achieve a high volumetric capacity of 55 Ah L⁻¹. Compared with some existing RFBs, the PhSSPh-based RFB has certain advantages in volumetric capacity and cell voltage (SI Appendix, Fig. S4). More interestingly, PhSSPh/CS₂ also shows an exceptional rate capability (Fig. 2D and SI Appendix, Fig. S5) (e.g., the capacity retention rate is 77% when the current density increases from 0.1 to 3.2 mA cm⁻², which is much greater than that of blank PhSSPh). A larger proportion (PhSSPh:CS₂ = 1:4) was also examined (SI Appendix, Fig. S6); the cyclic stability of PhSSPh was not further promoted. The electrochemical performance of the PhSSPh/CS₂ catholyte was further evaluated in a flow cell with 1.0 mL of catholyte injected (Fig. 2E). During 40 cycles of operation, the PhSSPh/CS₂ catholyte showed a high EE (>80%), and no capacity decay was observed, results that are better than those of PhSSPh alone (Fig. 2F).

Galvanostatic intermittent titration technique (GITT), which was successfully used to evaluate the redox kinetic processes of other organic active materials in RFBs (27), was applied to investigate the reaction kinetics of PhSSPh and PhSSPh/CS₂. The GITT curves of PhSSPh and PhSSPh/CS₂ are presented in Fig. 3A, 1 and 2, both show a similar quasi-equilibrium potential of ∼2.3 V. After a galvanic current of 0.05 mA cm⁻² was applied to the quasi-equilibrium potential, the voltage of PhSSPh/CS₂ in a representative plateau deviated from the quasi-equilibrium potential to ∼21 mV, which is much lower than the ∼102 mV of PhSSPh (Fig. 3A, 3). Cyclic voltammetry (CV) measurements were conducted to further understand their kinetic processes, as shown in Fig. 3B. Similar to the above galvanostatic voltage profiles, PhSSPh/CS₂ had smaller voltage separation than that of PhSSPh at different scan rates (Fig. 3C) (e.g., at a scan rate of 0.075 mV s⁻¹, the voltage separation of PhSSPh/CS₂ was 360 mV, which was less than the 660 mV of PhSSPh. The above results indicate that CS₂ can greatly facilitate the reaction kinetics of PhSSPh in RFBs.

¹³C NMR spectra and high-resolution mass spectrometry (HRMS) were conducted to reveal chemical transformations during the discharge/recharge of PhSSPh in RFBs. In the discharge process of PhSSPh, the characteristic peak of CS₂ at 193 ppm (purple shaded area) disappeared, and a new peak at 238 ppm (a) belonging to PhSCS₂Li was observed (Fig. 4A), which was also identified by HRMS (SI Appendix, Fig. S7), indicating that the C-S bond is formed during the discharge of PhSSPh. In the recharge process, the characteristic peak of CS₂ was detected again, and the peak at 238 ppm disappeared, meaning that the C-S bond was broken and CS₂ was unbound from PhSCS₂Li. After four cycles, the same results were also obtained (SI Appendix, Fig. S8). All in all, CS₂ was involved in the discharge of PhSSPh forming C-S bonds, and PhSCS₂Li was the discharged product. In the recharge, CS₂ and PhSSPh were reformed. This process was highly reversible, indicating CS₂ acted as a unique redox mediator. In addition, some CS₂ was bonded in the structure of PhSSPh to generate PhSCS₂Ph/PhSCS₂CS₂Ph, and the two molecules were detected by HRMS (Fig. 4 B and C). However, the characteristic peaks of these new molecules were not obviously observed in the NMR spectra, indicating that these molecules were present in small amounts. In other words, most CS₂ became unbound from PhSSPh at the end of recharge. For the anode side, there was no obvious difference in morphology between PhSSPh and PhSSPh/CS₂ as catholyte (SI Appendix, Fig. S9). In addition, the X-ray photoelectron spectroscopy (XPS) results for both were also similar (SI Appendix, Fig. S10), implying that there was not a large portion of CS₂ reacting with the lithium metal during cycling. Therefore, the existence of CS₂ had little effect on the lithium metal anode.

To understand the energy changes during these processes, the free energy profile containing the energetically low-lying intermediates and transition states was computed. First, PhSSPh⁺ underwent S-S bond breaking and overcame the energy barrier of 12.50 kcal mol⁻¹ to obtain Com⁺. Then, PhS⁺ was formed through
the dissociation of Ph$^+$ from Com$^-$ with a barrier of 10.10 kcal mol$^{-1}$. The energy barrier of the whole path of the S-S bond breakage of PhSSPh$^+$ to give a Ph$^+$ anion was 18.93 kcal mol$^{-1}$ (Fig. 4D). When CS$_2$ was coordinated to the outside of PhSSPh$^+$, intermediate IM1-CS$_2$*- containing a C-S bond was generated via the transition state TS1-CS$_2$*, with a barrier of 13.03 kcal mol$^{-1}$ (Fig. 4E). Subsequently, the S-S bond breakage of IM1-CS$_2$- through the transition state TS2-CS$_2$* occurred with a barrier of 10.03 kcal mol$^{-1}$ (relative to PhSSPh$^+$) to produce Com2-CS$_2$*-.

Finally, a PhCS$_2$*- anion was obtained by dissociation of Ph$^+$ from Com2-CS$_2$*- and was accompanied by an energy barrier of 13.03 kcal mol$^{-1}$ for the entire pathway. So, the addition of CS$_2$ can facilitate the cleavage of the S-S bond in PhSSPh by reducing about one-third of the energy barrier. For PhSSPh$^+$, the S-S bond via the complex states TSCS$_2$*- with a barrier of 6.55 kcal mol$^{-1}$ gave a complex ComCS$_2$-iso$^*$ (Fig. 4F). Then, a PhCS$_2$*- anion was obtained more easily by dissociating the Ph$^+$ radical from the isomer ComCS$_2$-iso$^*$ owing to the lower dissociation energy compared to that of PhSSPh$^+$. The overall free energy barrier for this catalytic cycle was only 8.8 kcal mol$^{-1}$ (from PhSSPh$^+$ to PhCS$_2$*- anion), showing that this reaction is energetically feasible. The whole path of the S-S bond breakage of PhSSPh$^+$ in $\text{CS}_2$ needs to overcome the free energy barrier of 7.46 kcal mol$^{-1}$ to form a PhCS$_2$*- anion (Fig. 4G). The above calculation results show that the S-S bond breakage of PhSSPh/CS$_2$ was more energetically feasible than that of PhSSPh, whether the CS$_2$ was outside or embedded in PhSSPh.

To prove the universality of our strategy, four other RSSR were selected (i.e., bis(3-fluorophenyl) disulfide [3FDS], bis(2-methyl-3-furyl) disulfide [MFDS], di-4-fluorophenyl sulfide [4FDS], and bis(4-methoxyphenyl) disulfide [MDS]). The potential differences in the four molecules were significantly reduced (Fig. 4H), and all of them with CS$_2$ exhibited high energy efficiencies and long-cycling performance (SI Appendix, Figs. S11–S14) (e.g., MFDS/CS$_2$ exhibited a low potential difference of 0.183 V and a capacity fading rate of 0.07% per cycle, which were better than those of MFDS with a high potential difference of 0.524 V and capacity fading rate of 0.21% per cycle). In short, CS$_2$ was proved to be an effective redox mediator to improve the redox kinetics of various RSSR, which makes CS$_2$ a potential candidate for various applications, such as lithium-oxygen batteries (Fig. 5A). In the latter, the redox mediator is positively charged lithium-oxygen batteries (Fig. 5A) was different from the ones reported for rechargeable lithium-oxygen batteries (Fig. 5B) (28, 29). In the latter, the redox mediator is positively charged lithium-oxygen batteries (Fig. 5A) was different from the ones reported for rechargeable lithium-oxygen batteries (Fig. 5B) (28, 29). In the latter, the redox mediator is positively charged lithium-oxygen batteries (Fig. 5A) was different from the ones reported for rechargeable lithium-oxygen batteries (Fig. 5B) (28, 29). In the latter, the redox mediator is positively charged lithium-oxygen batteries (Fig. 5A) was different from the ones reported for rechargeable lithium-oxygen batteries (Fig. 5B) (28, 29). In the latter, the redox mediator is positively charged lithium-oxygen batteries (Fig. 5A) was different from the ones reported for rechargeable lithium-oxygen batteries (Fig. 5B) (28, 29).
this process, a small amount of PhSCSC2Ph/PhSCSC2S2Ph with lower energy barriers was generated, which was also beneficial for accelerating reaction kinetics. The reversible C-S bond formation/breakage strategy shown here offers a perspective that enhances the electrochemical behavior of RSSR and greatly facilitates the development of organosulfide materials in energy storage applications.

Materials and Methods

Materials. PhSSPh (99%), 3FDS (97%), and MFDs (98%) were purchased from TCI. 4FDS (98%) was purchased from Alfa. MDS (98%) was purchased from Aladdin. CS2 (99.9%) was purchased from Adamas. A commercial ether-based electrolyte was purchased from Canad as the supporting electrolyte to explore the electrochemical performance of organosulfides, which consists of 1.0 M bis(trifluoromethanesulfonyl)imide lithium salt and 0.2 M lithium nitrate (LiNO3) in 1.2-dimethoxyethane/1,3-dioxolane. Lithium metal was purchased from China Energy Lithium Co., Ltd. Graphite felt with a thickness of 3 mm was purchased from Dalian Longtian Tech Co., Ltd. Carbon paper was purchased from NanoTech-Labs Composites, Inc. All chemicals were used directly without any further purification.

Assembly of a Lithium-Organosulfide Static Cell. A lithium-organosulfide static cell was assembled in the Ar-filled glove box ([H2O] < 0.01 ppm, [O2] < 0.01 ppm) as follows. First, an organosulfide-based catholyte was prepared by dissolving one organosulfide in the supporting electrolyte. Second, 15 μL catholyte was taken out and added into a carbon paper electrode with a diameter of 12 mm. Then, a piece of Celgard 2400 separator with a diameter of 19 mm was placed on the carbon paper, and 20 μL blank electrolyte was added to the separator. Finally, a piece of lithium metal with a diameter of 16 mm was placed on the blank electrolyte as the anode part.

Assembly of a Lithium-Organosulfide Flow Cell. A lithium-organosulfide flow cell was assembled as follows. First, a piece of lithium metal with a diameter of 20 mm as the anode, a Celgard 2400 separator (025 mm), a piece of graphite felt (020 × 3.0 mm), and a piece of carbon paper (020 mm) as the positive electrode were placed into a polytetrafluoroethylene flow channel (025 × 20 × 3.0 mm) in order. Then, 1.0 mL catholyte was injected into the polytetrafluoroethylene flow channel by a peristaltic pump. The current density for the flow cell was 1.0 mA cm−2.

Electrochemical Characterizations. A battery testing system (Neware, BTS-5V) was used to test cell performance. The cutoff voltages were set at 1.8 and 3.0 V. The GITT for battery discharge/charge was conducted from open circuit voltage to 1.8 V and then from 1.8 to 3.0 V at 0.05 mA cm−2 with a 10 min discharge/charge interval and 30 min delays. CV measurements were performed using a BioLogic VMP3 potentiostat. All cells were cycled 20 cycles at 0.2 mA cm−2 before the GITT and CV tests.

Characterization. 13C NMR spectra were recorded on a Bruker Ascend TM 600 MHz, and all samples were dissolved in dimethyl sulfoxide-d6. High-resolution mass spectrometry (HRMS) was recorded by an ultra-high-performance liquid chromatography (UPLC) quadrupole time-of-flight-MS system. The UPLC contained a Waters Acuity Plus system equipped with a photodiode array detector. Separation was obtained on the Waters Acuity UPLC BEH C18 column (2.1 mm × 100 mm, 1.7 μm). The solvent phase for UPLC was as follows: 100% acetonitrile at a flow rate of 0.2 mL min−1. HRMS analysis was performed on the Waters Xevo G2XS QToF mass spectrometer, which was connected to the UPLC system via an electrospray ionization interface. Mass accuracy and reproducibility were maintained by a Lockspray.

Density Functional Theory (DFT) Calculation. DFT calculation at MO62X/cc-pVZ level was implemented in the Gaussian 16 program (30). Frequency calculations were used to confirm the presence of local minima (no imaginary frequencies) and transition states (one imaginary frequency). Visualizations of all computed structures were created using the CYLview software package (31).

Data Availability. All study data are included in the article and/or SI Appendix.

ACKNOWLEDGMENTS. This work was supported by the National Natural Science Foundation of China (Grant Nos. U2004214, 21975225, and 51902293). We are grateful to the Supercomputing Center of the University of Science and Technology of China for providing computing resources.
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