Research Article

A Low-Crossover and Fast-Kinetics Thiolate Negolyte for Aqueous Redox Flow Batteries

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Aqueous redox flow batteries (ARFBs) are a promising technology for large-scale energy storage. Developing high-capacity and long-cycle negolyte materials is one of major challenges for practical ARFBs. Inorganic polysulfides are promising for ARFBs owing to its low cost and high solubility. However, it suffers from severe crossover resulting in low coulombic efficiency and limited lifespan. Organosulfides are more resistant to crossover than polysulfides owing to their bulky structures, but they suffer from slow reaction kinetics. Herein, we report a thiolate negolyte prepared by an exchange reaction between a polysulfide and an organosulfide, preserving low crossover rate of the organosulfide and high reaction kinetics of the polysulfide. The thiolate denoted as 2-hydroxyethyl disulfide+potassium polysulfide (HEDS+K2S2) shows reduced crossover rate than K2S2, faster reaction kinetics than HEDS, and longer lifespan than both HEDS and K2S2. The 1.5 M HEDS+1.5 M K2S2 static cell demonstrated 96 Ah L⁻¹ negolyte over 100 and 200 cycles with a high coulombic efficiency of 99.2% and 99.6% at 15 and 25 mA cm⁻², respectively. The 0.5 M HEDS+0.5 M K2S2 flow cell delivered a stable and high capacity of 30.7 Ah L⁻¹ negolyte over 400 cycles (691 h) at 20 mA cm⁻². This study presents an effective strategy to enable low-crossover and fast-kinetics sulfur-based negolytes for advanced ARFBs.

1. Introduction

The redox flow batteries (RFBs) are a promising energy storage technology owing to the decoupled power and energy, high scalability, and high safety compared to commercial Li-ion batteries [1–8]. Recently, sulfur-containing materials receive remarkable attention in both aqueous [9–13] and nonaqueous flow systems [14–21] owing to their low cost and high solubility compared with vanadium-based flow battery [22–25]. However, polysulfides suffer from severe crossover [7, 10, 12], which results in low coulombic efficiency and limited lifespan.

Previous studies have shown some effective methods to alleviate polysulfide crossover and improve coulombic efficiency. The transition metal sulfides [9, 11, 13] have been reported to function as both absorption layer and electrocatalysts for polysulfides. For example, Ma et al. [11] reported that nanostructured CoS₂/CoS on graphite felt shows obvious absorption and electrocatalytic effect for polysulfides. Gao et al. [13] reported that CuS was deposited on graphite felt electrode using successive ionic layer adsorption and reaction method, which absorbs polysulfides and promotes the redox reaction of the polysulfides. Membrane engineering is another way to alleviate crossover of polysulfides. Li et al. [10] and Ma et al. [11] employed two layers of membranes (Nafion) to mitigate the crossover of polysulfides thereby improving coulombic efficiency. Gross and Manthiram [12] further applied a solid-electrolyte NASICON (Na₃Zr₂Si₂PO₁₂) and LATP (Li₁ₓAlₓTi₂₋ₓP₃₋ₗSi₈O₁₂) to eliminate chemical crossover and enhance battery cycle life. Recently, Li and Lu [26] designed a charge-reinforced ion-selective (CRIS) membrane to retain polysulfide/polyiodide, achieving a superior stable cycling of 17.9 Ah L⁻¹ negolyte+posolyte over 500 cycles.

Organosulfides [19, 20, 27–31] are attractive materials in energy storage owing to their high theoretical capacity, high structure diversity, and environmental friendliness. The S-S bond is reversibly broken and reformed upon cycling, involving two-electron transfer [32, 33]. Compared with inorganic polysulfides, organosulfides exhibit reduced
crossover owing to their bulky molecular structures. However, the reaction kinetics of organosulfides is much slower than inorganic polysulfides due to their high S-S bond dissociation energy [27, 34–36].

Herein, we report a thiolate negolyte prepared by an exchange reaction between a polysulfide and an organosulfide for aqueous RFBs, preserving low crossover rate of the organosulfide and high reaction kinetics of the polysulfide. UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), and electrospray ionization mass spectra (ESI-MS) techniques were used to confirm the formation of thiolate from the exchange reaction between polysulfides and organosulfides. The thiolate denoted as 2-hydroxyethyl disulfide-potassium polysulfide (HEDS+K₂S₂) shows reduced crossover rate than K₂S₂, faster reaction kinetics than HEDS, and longer lifespan than both HEDS and K₂S₂. The 1.5 M HEDS+1.5 M K₂S₂ static cell demonstrated 96 Ah L⁻¹ negolyte over 100 and 200 cycles with a high coulombic efficiency of 99.2% and 99.6% at 15 and 25 mA cm⁻², respectively. The 0.5 M HEDS+0.5 M K₂S₂ flow cell delivered a stable and high capacity of 30.7 Ah L⁻¹ over 400 cycles (691 h) at 20 mA cm⁻². This study presents an effective strategy to enable low-crossover and fast kinetics sulfur-based negolytes for advanced aqueous RFBs.

2. Materials and Methods

2.1. Materials. Potassium iodide (KI, ≥99%), potassium (poly)sulfide (K_S₄, ≥42% K_S₃ basis, x is determined to be ~2 [10]), potassium chloride (KCl, ≥99.0%), potassium hydroxide (KOH, ≥85%), and sulfuric acid (H₂SO₄, 95–98%) were received from Sigma-Aldrich. Hydrogen peroxide (H₂O₂, 30 wt% in H₂O) was received from Dikeman, Shenzhen. 2-Hydroxyethyl disulfide was received from Alfa Aesar. Graphite felt (GFs, Φ16 mm, thickness: 3 mm) was received from Shanghai Sanshe Polysul Machinery Technology Co., Ltd. Nickel foam was boiled in 1 M K₂S₂ solution in air for 6 h to increase hydrophobicity. GFs were heated in a furnace (YFK60X300/120 K-GC, Shanghai Y-Feng Electrical Furnace Co., Ltd., China) at 550°C in air for 6 h to increase hydrophobicity. The CuS-coated GFs were fabricated as followed. The CuS particles were mixed with ketjenblack and poly(vinylidene difluoride) binder in NMP to form a uniform slurry at a weight ratio of 8:1:1. Then, the slurry was coated onto GFs and dried in vacuum at 80°C overnight. The loading of CuS was 20-25 mg cm⁻² in static cells and 30-35 mg cm⁻² in flow cells. The K⁺ Naion membranes were pretreated with the following steps: (i) Naion membranes were soaked in 5 wt% H₂O₂ aqueous solution at 80°C for 1 h and then rinsed with deionized (DI) water for 6-8 times; (ii) the membranes were soaked in 5% H₂SO₄ at 80°C for 1 h followed by DI water rinsing for 6-8 times; (iii) the membranes were soaked in 1 M KOH aqueous solution at 80°C for 2 hours to covert from the H⁺-form to the K⁺-form. Then, the membranes were rinsed with DI water again and stored in DI water. For static cell assembly, two stacked nickel foam (Φ16 mm) or a CuS-coated GF (Φ 16 mm, thickness: 1.5 mm) was used as the negative electrode and a GF (Φ 16 mm, thickness: 3 mm) was used as the positive electrode, separated by the Naion 117 membrane (active area of 6 cm²). 150 μL negolyte and 500 μL posolyte were used. Additional 80 μL DI water was added on the negative electrode to keep a good wettability. The negolytes with different concentration were prepared by dissolving polysulfide, HEDS in 1 M KOH solution. KI posolytes were prepared by dissolving KI into DI water. DI water was continuously bubbled with argon gas for 15 min before the use. All electrolytes were prepared at room temperature in an Ar-filled glove box (Etelux, H₂O < 1.0 ppm, O₂ < 1.0 ppm).

Briefly, flow cells were comprised of poly(tetrafluoroethylene) (PTFE) frame, graphite plates as current collector on each side, and two nickel foams (12 cm²) or a CuS-coated GF (12 cm²) as the negative electrode and a GF (12 cm²), thickness: 3 mm) as the positive electrode sandwiching two Naion 117 membranes (39 cm²). The negolyte volume of 2 M "sulfur" (i.e., 1 M HEDS or 1 M K₂S₂ or 0.5 M HEDS+0.5 M K₂S₂) is 6.5 mL with 22 mL 1.5 M KI posolyte. The negolyte volume of 1.5 M HEDS+1.5 M K₂S₂ is 4 mL with 15 mL 5 M KI posolyte. The flow rate of pumps was 70 mL min⁻¹. Both the static cells and flow cells were sealed in Ar-filled glove box and tested in air. This is because the thiolate (HO-CH₂-CH₂-S-K⁺) could be oxidized to HO-CH₂-CH₂-S-SO₂⁻K⁺ by oxygen considering the thiol (R-S-S-H) is reported to be oxidized to R-S-SO₂⁻H by oxidizing agents [37, 38].

2.2. Assembly of Aqueous Thiolate, Organosulfide, and Polysulfide-Iodide Redox Flow Batteries. Before battery assembly, pretreatments of nickel foams (Φ 16 mm, thickness: 1.5 mm), graphite felts (GFs, Φ 16 mm, thickness: 3 mm), and Naion 117 membranes (active area of 6 cm²) were conducted. Nickel foams were boiled in 1 M K₂S₂ solution for 5 h at 100°C until the color turned black uniformly. Then, they were dried under dynamic vacuum overnight at 80°C in a glass oven (Büchi, Switzerland) to prevent the oxidation of oxygen. GFs were heated in a furnace (YFK60X300/120 K-GC, Shanghai Y-Feng Electrical Furnace Co., Ltd., China) at 550°C in air for 6 h to increase hydrophilicity. The CuS-coated GFs were fabricated as followed. The CuS particles were mixed with ketjenblack and poly(vinylidene difluoride) binder in NMP to form a uniform slurry at a weight ratio of 8:1:1. Then, the slurry was coated onto GFs and dried in vacuum at 80°C overnight. The loading of CuS was 20-25 mg cm⁻² in static cells and 30-35 mg cm⁻² in flow cells. The K⁺ Naion membranes were pretreated with the following steps: (i) Naion membranes were soaked in 5 wt% H₂O₂ aqueous solution at 80°C for 1 h and then rinsed with deionized (DI) water for 6-8 times; (ii) the membranes were soaked in 5% H₂SO₄ at 80°C for 1 h followed by DI water rinsing for 6-8 times; (iii) the membranes were soaked in 1 M KOH aqueous solution at 80°C for 2 hours to covert from the H⁺-form to the K⁺-form. Then, the membranes were rinsed with DI water again and stored in DI water. For static cell assembly, two stacked nickel foam (Φ 16 mm) or a CuS-coated GF (Φ 16 mm, thickness: 1.5 mm) was used as the negative electrode and a GF (Φ 16 mm, thickness: 3 mm) was used as the positive electrode, separated by the Naion 117 membrane (active area of 6 cm²). 150 μL negolyte and 500 μL posolyte were used. Additional 80 μL DI water was added on the negative electrode to keep a good wettability. The negolytes with different concentration were prepared by dissolving polysulfide, HEDS in 1 M KOH solution. KI posolytes were prepared by dissolving KI into DI water. DI water was continuously bubbled with argon gas for 15 min before the use. All electrolytes were prepared at room temperature in an Ar-filled glove box (Etelux, H₂O < 1.0 ppm, O₂ < 1.0 ppm).

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2.3. Electrochemical Measurements. Cyclic voltammogram tests of K₂S₂, HEDS, HEDS+K₂S₂, and KI were conducted using a glassy carbon as the working electrode, a platinum gauze as the counter electrode, and a saturated-calomel reference electrode (SCE) as the reference electrode by Biologic. The CVs of KI were investigated in Figure S1, showing two redox reactions, involving I⁻/I₃⁻ couple at 0.2-0.6 V vs. SCE and I⁻/I₂ couple at 0.6-0.9 V vs. SCE. I⁻/I₃⁻ redox couple was employed in the flow battery to prevent the precipitation of iodine on cathode [10]. KI exhibits much smaller peak separation (e.g., 0.40 V/0.52 V at 10 mV s⁻¹) compared to the negolytes (HEDS, K₂S₂, and HEDS+K₂S₂), indicating the fast reaction kinetics. To improve the kinetics of the thiolate, nickel foam was further used as negative electrode in full cell tests owing to the electrocatalytic effect of NiS₂ on nickel foam [10, 39],
where NiS\(_2\) was identified by X-ray powder diffraction (XRD) as shown in Figure S2. Galvanostatic discharge/charge tests (static cell) were conducted with 0.4–1.6 V at 10 mA cm\(^{-2}\) with one Nafion 117 membrane. For rate performance tests, the cutoff voltage was 0.4–1.6 V with the rate ranging from 5 to 15 mA cm\(^{-2}\) and 0.2–1.8 V at 20 and 25 mA cm\(^{-2}\) with one Nafion 117 membrane. The cycling performance tests (static cell) were conducted with 0.4–1.6 V at 15 mA cm\(^{-2}\) and 0.2–1.8 V at 25 mA cm\(^{-2}\) with two Nafion 117 membranes. Galvanostatic discharge/charge tests (flow cell) were conducted with 0.4–1.7 V at 20 mA cm\(^{-2}\) with two Nafion 117 membranes. The upper limit of the charging process was limited by the cutoff voltage or the designated state of charge (SOC).

2.4. Characterization. The UV-vis spectroscopy (SEC2000; ALS; Japan) was switched on 30 min before the test. The UV-vis data were collected every 0.5 s. The blank electrolyte consists of 1 M KCl in H\(_2\)O. Fourier transform infrared spectroscopy (FTIR) was recorded with an ALPHA FTIR instrument (Bruker, Germany) in ATR mode. Electrotransformation ionization mass spectra (ESI-MS) were collected using a Q Exactive Focus Hybrid Quadrupole-Orbitrap Mass Spectrometer with HESI II source in negative ion mode. XRD tests were performed using an X-ray diffractometer (SmartLab) with Cu K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)). The angle range was 20°–80° at 5° min\(^{-1}\) for nickel foams and 30°–40° at 0.5° min\(^{-1}\) for GFs. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a JSM-7800F field emission scanning electron microscope (JEOL, Japan). The GFs for SEM/EDX were obtained after 20 cycles for 3 M HEDS, 3 M K\(_2\)S\(_2\), and 1.5 M HEDS+1.5 M K\(_2\)S\(_2\) negolytes coupled with 5 M KI posolyte at static mode (SOC = 60%) at 15 mA cm\(^{-2}\) with one Nafion 117. The GFs were rinsed for 5–8 times with DI water to dissolve soluble KI.

3. Results

3.1. Electrochemical Properties of 2-Hydroxyethyl Disulfide. Solubility is one of the most important factors determining the energy density of the negolyte. To maximize the solubility of organosulfide in water electrolyte, we select 2-hydroxyethyl disulfide (HEDS) which has a hydroxy (–OH) group at the terminal carbon. HEDS shows a maximum solubility of \(~8\) M (only liquid HEDS as an electrolyte), corresponding to a theoretical capacity of 429 Ah L\(^{-1}\) negolyte, which has a strong advantage compared to other organic active materials in aqueous redox flow batteries (Table S1). To evaluate HEDS under high concentration, 5 M KI posolyte was used to couple with different concentrations of HEDS negolytes (3 M, 5 M, and 8 M). Figure 1(a) shows that HEDS exhibited a high capacity of 79.9, 132.4, and 211.9 Ah L\(^{-1}\) negolyte at the concentration of 3 M, 5 M, and 8 M at 10 mA cm\(^{-2}\) at 50% state of charge (SOC). In addition, a high coulombic efficiency (CE) was achieved, corresponding to 99.4% (3 M), 98.7% (5 M), and 98.7% (8 M), suggesting the low crossover of HEDS under high concentration. However, the HEDS cells at all concentrations exhibit a large voltage hysteresis (~470 mV).

3.2. Formation of Thiolate via Exchange Reactions. To improve the reaction kinetics of organosulfoxides, we utilize exchange reaction [19, 40, 41] to prepare the thiolate as active material, which is expected to possess the merits of both organosulfides (low crossover) and inorganic polysulfides (faster kinetics than organosulfides) as shown in equation (1). The thiolate also involves two-electron reaction as shown in equation (2).

\[
\begin{align*}
\text{HO} - \text{CH}_2 - \text{CH}_2 - S - S - \text{CH}_2 - \text{CH}_2 - \text{OH} + \text{K}_2\text{S}_2 & \rightarrow 2\text{HO} - \text{CH}_2 - \text{CH}_2 - S - S^- + \text{OH}^- + 2\text{K}^+ \ (1) \\
\text{HO} - \text{CH}_2 - \text{CH}_2 - S - S^- + 2e^- & \rightarrow \text{HO} - \text{CH}_2 - \text{CH}_2 - S^- + S^{2-} \ (2)
\end{align*}
\]

The preparation of thiolate was achieved by mixing equimolar of HEDS and K\(_2\)S\(_2\) in water. The UV-vis spectra showed the absorption peaks of S\(^2-\) (260 nm [10, 42]), S\(_2\)^{2-} (300 nm [10, 42, 43]), and S\(_2\)/S\(_4\)^{2-} (370 nm [10, 42, 43]) species for K\(_2\)S\(_2\), suggesting K\(_2\)S\(_2\) solution is a mixture of multiple polysulfides owing to the self-disproportionation reaction of the polysulfides [10] as shown in Figure 1(b). In contrast, HEDS shows one absorption peak at 247 nm without other fragments of polysulfides. Interestingly, when mixing the equimolar of HEDS with K\(_2\)S\(_2\), the intensity of S\(_2\)/S\(_4\)^{2-} (300 nm) and S\(_2\)/S\(_4\)^{2-} (370 nm) significantly decreased, indicating the transformation of polysulfides with much reduced self-disproportionation reactions. We then use FTIR technique to investigate the change of functional group before and after the exchange reaction of HEDS and K\(_2\)S\(_2\), Figure 1(c) shows that HEDS has the strong peak at 1043 cm\(^{-1}\) attributing to C-O stretching and two weak peaks (2924 cm\(^{-1}\), 2873 cm\(^{-1}\)) attributing to CH\(_2\) stretching. HEDS +K\(_2\)S\(_2\) shows a weaker C-O stretching peak compared with HEDS owing to half number of C-O bond. And the CH\(_2\) stretching disappears in the mixture of HEDS+K\(_2\)S\(_2\) which is attributed to the half number of CH\(_2\) compared to HEDS.

We note that the molecular structure of HEDS is stable in water and hydroslysis reaction does not occur for HEDS (Figure S3). To further confirm the formation of thiolate, we conducted electrospray ionization mass spectra (ESI-MS) to investigate the anions in the solution. As shown in Figure 1(d), HEDS+K\(_2\)S\(_2\) showed a strong HO(CH\(_2\))\(_2\)S\(_2\)^{-} signal at m/z = 108.9788 signal of about four times than that of HEDS. The weak HO(CH\(_2\))\(_2\)S\(_2\)^{-} signal in HEDS could be attributed to the C-S bond cleavage of HEDS molecule during the ionization process. In contrast, the strong HO(CH\(_2\))\(_2\)S\(_2\)(CH\(_2\))\(_2\)O^- signal at m/z = 153.0047 appears in HEDS while disappears in the mixture of HEDS+K\(_2\)S\(_2\). Trace (HO(CH\(_2\))\(_2\)S\(_2\))\(^2+\) signal at m/z = 154.0126 was detected in both, which is twice in HEDS than HEDS+K\(_2\)S\(_2\). These observations show that the new thiolate species is successfully prepared after the exchange reaction between HEDS and K\(_2\)S\(_2\). The full m/z range of ESI-MS spectra is shown in Figure S4.
3.3. Electrochemical Properties of the Thiolate Negolyte. To understand electrochemical property difference of the thiolate and precursors (HEDS and K₂S₂), we performed three-electrode CVs using glassy carbon as the working electrode, platinum gauze as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. HEDS shows a very weak reduction/oxidation peak pair and a large peak separation as shown in Figure S5a, indicating poor electrochemical activity. It shows a reduction peak at ~-0.94 V vs. SCE and an oxidation peak at ~0V at 10 mV s⁻¹. In contrast, K₂S₂ exhibits a strong reduction/oxidation peak pair and a large peak separation as shown in Figure S5a, indicating poor electrochemical activity. It shows a reduction peak at ~-0.94 V vs. SCE and an oxidation peak at ~0V at 10 mV s⁻¹. In contrast, K₂S₂ exhibits a strong reduction/oxidation peak pair and a large peak separation as shown in Figure S5a, indicating poor electrochemical activity. It shows a reduction peak at ~-0.94 V vs. SCE and an oxidation peak at ~0V at 10 mV s⁻¹. HEDS+K₂S₂ shows a strong reduction peak at ~-0.85 V and two oxidation peaks at ~-0.20 V and ~-0.05 V at 10 mV s⁻¹. The reduction peak could be attributed to the two-electron transfer from HO(CH₂)₂S₂⁻ (or HO(CH₂)₂S·S⁻) to HO(CH₂)₂S⁻ and S²⁻. The oxidation peak at ~-0.2 V and ~-0.07 V could be attributed to the oxidation process of S²⁻ → S·⁻ and HO(CH₂)₂S → HO(CH₂)₂S²⁻, respectively. During CV cycling at 100 mV s⁻¹ (Figure S5d–f), the reduction/oxidation peak intensity of K₂S₂ decreases clearly from the 10th cycle to the 800th cycle (Figure S5e). In contrast, the reduction/oxidation peak intensity of HEDS+K₂S₂ remained stable without obvious decay from the 10th cycle to the 800th cycle, suggesting the higher cycling stability of HEDS+K₂S₂ than that of individual K₂S₂. The redox peaks disappear at high scan rate (100 mV s⁻¹) for HEDS owing to the poor electrochemical activity.

Figure 1: (a) Galvanostatic discharge-charge profiles of HEDS (3 M, 5 M, and 8 M)/5 M KI static cell at 10 mA cm⁻² at SOC = 50%. (b) UV-vis spectra of K₂S₂, HEDS, and HEDS+K₂S₂. (c) FTIR spectra of HEDS, K₂S₂, and HEDS+K₂S₂. (d) Mass spectra intensity at specified ion peaks for HEDS and HEDS+K₂S₂.
HEDS and K$_2$S$_2$ in the full cell, we coupled 5 M KI posolyte with these negolytes and conducted galvanostatic charge-discharge tests at 10 mA cm$^{-2}$ at SOC = 100% of negolytes (Figure 2(a)). First, all negolytes reached >93.1% of theoretical capacity, suggesting a reversible reaction of polysulfide, organosulfide, and thiolate. Second, K$_2$S$_2$ shows the highest discharge voltage of 0.94 V and the smallest voltage hysteresis (197 mV) followed by HEDS+K$_2$S$_2$ (discharge voltage: 0.83 V/voltage hysteresis: 280 mV) and HEDS (discharge voltage: 0.78 V/voltage hysteresis: 354 mV), indicating the reaction kinetics is in the order of K$_2$S$_2$ > HEDS +K$_2$S$_2$ > HEDS. Third, HEDS achieved the highest CE of 98.5% followed by HEDS+K$_2$S$_2$ (96.7%) and K$_2$S$_2$ (93.1%), suggesting the crossover is in the order of HEDS < HEDS+K$_2$S$_2$ < K$_2$S$_2$. The lower crossover rate of the thiolate than K$_2$S$_2$ can be attributed to its larger molecular size.

A self-discharge test was conducted after the 2nd charge (SOC = 100%) to evaluate the crossover rate of these negolytes. As shown in Figure 2(b), 3 M HEDS shows the longest self-discharge time (352 h) to reach the open-circuit voltage (OCV) of 0.5 V followed by 1.5 M HEDS+1.5 M K$_2$S$_2$ (243 h) and 3 M K$_2$S$_2$ (74 h). Considering the same concentration of KI (5 M) in posolyte, the crossover of sulfur species across the membrane is the main contribution of causing different self-discharge time. The self-discharge test suggests that HEDS shows a much reduced crossover rate compared to the thiolate (HEDS+K$_2$S$_2$) followed by K$_2$S$_2$. In addition, the concentration has a strong effect on the self-discharge time. For instance, the 3 M K$_2$S$_2$ shows a shorter self-discharge time (74 h) than 1.5 M K$_2$S$_2$ (102 h) owing to higher concentration gradient. Interestingly, 1.5 M HEDS+1.5 M K$_2$S$_2$ exhibited 2.4 times longer self-discharge time than 1.5 M K$_2$S$_2$, indicating the greatly alleviated crossover of the thiolate.

3.4. Electrochemical Performance and Self-Discharge Test of Polysulfide, Organosulfide, and Thiolate Cells. To evaluate the electrochemical performance of HEDS, K$_2$S$_2$, and HEDS+K$_2$S$_2$ in the full cell, we coupled 5 M KI posolyte with these negolytes and conducted galvanostatic charge-discharge tests at 10 mA cm$^{-2}$ at SOC = 100% of negolytes (Figure 2(a)). First, all negolytes reached >93.1% of theoretical capacity, suggesting a reversible reaction of polysulfide, organosulfide, and thiolate. Second, K$_2$S$_2$ shows the highest discharge voltage of 0.94 V and the smallest voltage hysteresis (197 mV) followed by HEDS+K$_2$S$_2$ (discharge voltage: 0.83 V/voltage hysteresis: 280 mV) and HEDS (discharge voltage: 0.78 V/voltage hysteresis: 354 mV), indicating the reaction kinetics is in the order of K$_2$S$_2$ > HEDS +K$_2$S$_2$ > HEDS. Third, HEDS achieved the highest CE of 98.5% followed by HEDS+K$_2$S$_2$ (96.7%) and K$_2$S$_2$ (93.1%), suggesting the crossover is in the order of HEDS < HEDS+K$_2$S$_2$ < K$_2$S$_2$. The lower crossover rate of the thiolate than K$_2$S$_2$ can be attributed to its larger molecular size.

A self-discharge test was conducted after the 2nd charge (SOC = 100%) to evaluate the crossover rate of these negolytes. As shown in Figure 2(b), 3 M HEDS shows the longest self-discharge time (352 h) to reach the open-circuit voltage (OCV) of 0.5 V followed by 1.5 M HEDS+1.5 M K$_2$S$_2$ (243 h) and 3 M K$_2$S$_2$ (74 h). Considering the same concentration of KI (5 M) in posolyte, the crossover of sulfur species across the membrane is the main contribution of causing different self-discharge time. The self-discharge test suggests that HEDS shows a much reduced crossover rate compared to the thiolate (HEDS+K$_2$S$_2$) followed by K$_2$S$_2$. In addition, the concentration has a strong effect on the self-discharge time. For instance, the 3 M K$_2$S$_2$ shows a shorter self-discharge time (74 h) than 1.5 M K$_2$S$_2$ (102 h) owing to higher concentration gradient. Interestingly, 1.5 M HEDS+1.5 M K$_2$S$_2$ exhibited 2.4 times longer self-discharge time than 1.5 M K$_2$S$_2$, indicating the greatly alleviated crossover of the thiolate.

3.5. Coulombic Efficiency and Energy Efficiency at Various Rates. We evaluated the coulombic efficiency and energy efficiency of 3 M K$_2$S$_2$, 3 M HEDS, and 1.5 M HEDS+1.5 M K$_2$S$_2$ at SOC = 60% at various rates (static mode). First, all negolytes showed improved CE with the increase of current density. For instance, HEDS and HEDS+K$_2$S$_2$ showed significantly higher CE than K$_2$S$_2$ and the difference in CE is especially large at low current density. For instance, HEDS and HEDS+K$_2$S$_2$ exhibited a high CE of 98.1% and 96.9% at 5 mA cm$^{-2}$ while K$_2$S$_2$ showed a low CE of 91.3%. HEDS and HEDS+K$_2$S$_2$ showed a high CE of 99.3% and 99.4% compared to 96.6% of K$_2$S$_2$. These trends in energy efficiency (EE) are reversed. K$_2$S$_2$ showed the highest EE in the order of negolytes, which is 83.5%, 81.7%, 74.2%, 67.6%, and 60.9% from 5 to 25 mA cm$^{-2}$. The EE of HEDS+K$_2$S$_2$ is comparable to that of K$_2$S$_2$, exhibiting 84.4%, 77.7%, 71.1%, 65.0%, and 59.2% from 5 to 25 mA cm$^{-2}$. The EE results are consistent with our hypothesis that the crossover of the organosulfide and thiolate is slower compared to polysulfide in the order of HEDS < HEDS+K$_2$S$_2$ < K$_2$S$_2$. The trend in energy efficiency (EE) is reversed. K$_2$S$_2$ showed the highest EE among the negolytes, which is 83.5%, 81.7%, 74.2%, 67.6%, and 60.9% from 5 to 25 mA cm$^{-2}$.

3.6. Morphology of Graphite Felts after Cycling. To understand how negolyte crossover affects the positive electrode (graphite felt) morphology, we performed scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/
EDX) images of graphite felt after cycling (Figure 4). As shown in Figure 4(b), the graphite felt surface of the cell with K₂S₂ negolyte was passivated by a thick film containing sulfur element. The deposition was further verified by XRD characterization to be elemental sulfur (Figure S7). This sulfur deposition on graphite felt resulted from severe
crossover of polysulfide, which is consistent with the short self-discharge time (Figure 2(b)) and low coulombic efficiency (Figure 3(b)). Furthermore, the high brightness of the thick film is consistent with the poor electrical conductivity of elemental sulfur. In contrast, the graphite felts cycled in the cells using HEDS and HEDS+K$_2$S$_2$ negolytes were free of sulfur deposition, which is consistent with reduced crossover. A further broad view is shown in Figure S8. The EDX mapping shows traces of sulfur element on the graphite felt for HEDS and HEDS+K$_2$S$_2$, which could come from the manufacturing process of graphite felt, as evidenced from the SEM/EDX of pure graphite felt (Figure S9).

3.7. Cycling Performance under Static and Flow Mode. We first performed cycling stability at 15 mA cm$^{-2}$ with two Nafion 117 membranes to minimize the crossover of active materials at static mode. SOC was chosen as 60%, which is reasonable for aqueous polysulfide flow batteries [10, 11]. First, all negolytes exhibited a high discharge capacity of 96 Ah L$^{-1}$ negolyte, demonstrating high reversibility of the organosulfide, polysulfide, and thiolate under such a high concentration (6 M “sulfur”). K$_2$S$_2$ decayed after cycling for 30 cycles (Figure 5(a)), which could result from severe crossover of polysulfides and sulfur passivation on positive electrode surface. HEDS showed comparable cycling performance with K$_2$S$_2$, demonstrating 50 stable cycles before capacity decay. The poor cycling performance of HEDS may result from poor electrochemical activity. Interestingly, HEDS+K$_2$S$_2$ showed a stable cycling over 100 cycles, which is more stable than individual HEDS and K$_2$S$_2$ negolytes. Benefiting from less crossover and improved kinetics, HEDS+K$_2$S$_2$ achieved a high CE (~99.2%) and reasonable EE (~59.4%) compared to HEDS (CE: ~99.1%, EE: ~52.9%) and K$_2$S$_2$ (CE: ~97.7%, EE: ~65.3%) as shown in Figures 5(b) and 5(c). Figure S10 shows the galvanostatic voltage profiles of HEDS+K$_2$S$_2$, HEDS, and K$_2$S$_2$ at 15 mA cm$^{-2}$. The static cells were further evaluated at a higher rate of 25 mA cm$^{-2}$ (Figure S11). A stable cycling over 200 cycles was achieved for HEDS+K$_2$S$_2$ with a high CE of 99.6% with no capacity loss. In contrast, K$_2$S$_2$ and HEDS decayed sharply after a stable cycling over 50 cycles and 70 cycles with corresponding CE of 97.4% and 99.1%, respectively.

To test cycling stability of HEDS, K$_2$S$_2$, and HEDS+K$_2$S$_2$ at flow mode, we assembled flow cells under a moderate concentration of 2 M “sulfur,” which is 0.5 M HEDS+0.5 M K$_2$S$_2$, 1 M K$_2$S$_2$, and 1 M HEDS. The SOC is 60% for negolyte side. First, 0.5 M HEDS+0.5 M K$_2$S$_2$ showed better cycling performance than the precursors (1 M HEDS and 1 M K$_2$S$_2$) as shown in Figures 5(d)–5(f). It displayed a stable 30.7 Ah L$^{-1}$ negolyte over 400 cycles (691 h) at 20 mA cm$^{-2}$ with an average CE of 99.5%. In contrast, 1 M K$_2$S$_2$ showed 28.9 Ah L$^{-1}$ negolyte at 20 mA cm$^{-2}$ over 217 cycles (375 h) with an average CE of 99.0% and the capacity decay was obviously observed after 210 cycles. We note that 1 M K$_2$S$_2$ showed a high average CE of 99.0% compared to 97.7% in 3 M K$_2$S$_2$ (Figure 5(b)), indicating less severe crossover of
K_2S_2 at a relatively low concentration (1 M). 1 M HEDS exhibited 25.8 Ah L^{-1} negolyte at 20 mA cm^{-2} after 75 cycles (129 h) with an average CE of 98.0%. The capacity and CE of 1 M HEDS dropped obviously after 66 cycles. The poor cycling performance of HEDS is consistent with the poor electrochemical activity as shown in Figures S5a and S5d. The individual HEDS may encounter side reactions during cycling test. Further studies on the degradation mechanism of HEDS are needed. The flow cell results show that HEDS+K_2S_2 exhibited much improved cycling stability compared to HEDS and K_2S_2, which is consistent with the CV results (Figure S5). The galvanostatic voltage profiles are shown in Figure S12. We then examine cycling stability and coulombic efficiency at a higher concentration of 1.5 M HEDS+1.5 M K_2S_2 at flow mode as shown in Figure S13. It exhibits a high volumetric capacity of 96.1 Ah L^{-1} negolyte with a high coulombic efficiency of 99.4% over 75 cycles (240 h).

To further improve the reaction kinetics of HEDS+K_2S_2 and reduce electrode material cost, we employed CuS-coated [13] graphite felt as an electrode to replace the pretreated nickel foam (Figure 6). Both CuS-coated graphite felt and pretreated nickel foam showed stable cycling over 100 cycles at 15 mA cm^{-2} at static mode at SOC = 60%. Interestingly, CuS-coated graphite felt exhibited a higher energy efficiency of 69.7% over 100 cycles at 15 mA cm^{-2} compared to 59.4% of pretreated nickel foam (Figure S14). Figure 6(b) shows CuS-coated graphite felt showed smaller voltage hysteresis (333 mV) than pretreated nickel foam (482 mV). The galvanostatic discharge-charge profile is shown in Figure 6(c). The rate capability of CuS-coated
graphite felt is shown in Figure S15, suggesting faster kinetics of CuS-coated graphite felt than pretreated nickel foam at 5-25 mA cm⁻². Furthermore, 1.5 M HEDS+1.5 M K₂S₂ flow cell with CuS-coated graphite felt showed a stable cycling performance over 75 cycles (240 h) with a relatively high energy efficiency of 61.8% at 20 mA cm⁻², compared to the low energy efficiency of 49.1% of pretreated nickel foam in Figure 6(d). The capacity retention and selected galvanostatic charge-discharge profiles of CuS-coated graphite felt are shown in Figure S16. The catalytic mechanism of transition metal sulfides on organosulfides/thiolytes redox reaction needs to be further investigated.

4. Discussion

In summary, we demonstrated a new thiolyte negolyte for aqueous redox flow batteries obtained via the exchange reaction between a polysulfide and an organosulfide. The thiolyte negolyte (HEDS+K₂S₂) exhibits high capacity, low self-discharge, and long cycle life. Interestingly, the HEDS+K₂S₂ shows reduced crossover rate than K₂S₂, faster reaction kinetics than HEDS, and longer lifespan than both HEDS and K₂S₂. The 1.5 M HEDS+1.5 M K₂S₂ static cell demonstrated 96 Ah L⁻¹negolyte over 100 and 200 cycles with a high coulombic efficiency of 99.2% and 99.6% at 15 and 25 mA cm⁻², respectively. The 0.5 M HEDS+0.5 M K₂S₂ flow cell delivered a stable and high capacity of 30.7 Ah L⁻¹negolyte over 400 cycles (691 h) at 20 mA cm⁻². This study presents an effective strategy to enable low-crossover and fast-kinetis sulfur-based negolytes for advanced aqueous RFBs.

Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper and the Supplementary Materials. Additional data related to this paper may be requested from the corresponding authors.

Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

B. Y. and Y.-C. L. were responsible for conceptualization. B. Y., Z. W., and W. W. were responsible for methodology. B. Y. was responsible for investigation. B. Y. was responsible for writing—original draft. B. Y., Z. W., W. W., and Y.-C. L. were responsible for writing—review and editing.

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Supplementary Materials

Supplementary Figure S1: cyclic voltammetry (CV) of 10 mM KI. (a) Voltage window in 0.2-0.9 V and 0.3-0.65 V. (b) Scan rates from 5 to 200 mV s⁻¹. (c) Cycling stability at 100 mV s⁻¹. (d) Cycling stability at 200 mV s⁻¹. Figure S2: (a) XRD and (b) photograph of nickel foam before and after treatment. Ni: PDF#04-0850; NiS₂: PDF#11-0099. Table S1: characteristics of the state-of-the-art redox active negolytes for aqueous flow batteries. Figure S3: FTIR spectra of 3 M HEDS and pure HEDS. Figure S4: ESI-MS spectra of (a) HEDS, (b) K₂S₂, and (c) HEDS+K₂S₂. The “*” indicates the mutual species in the three electrolytes, which could result from atmosphere and electrolyte itself. Figure S5: CV of (a) 5 mM HEDS, (b) 5 mM K₂S₂, and (c) 5 mM HEDS+5 mM K₂S₂ at 5.0 M KCl. CV at the 10th, 200th, 400th, 600th, and 800th cycles of (d) 5 mM HEDS, (e) 5 mM K₂S₂, and (f) 5 mM HEDS+5 mM K₂S₂ at 100 mV s⁻¹. Figure S6: rate capability of 3 M HEDS, 3 M K₂S₂, and 1.5 M HEDS+1.5 M K₂S₂ at 5-25 mA cm⁻² in static mode in (a) coulombic efficiency, (b) energy efficiency, and (c) voltage efficiency. Figure S7: XRD pattern of carbon felts for HEDS, K₂S₂, and HEDS+K₂S₂ in a narrow range of 30-40°. Figure S8: SEM image of carbon felt for (a) pristine HEDS, (b) CuS-coated graphite felt, and (d) HEDS+K₂S₂ in a low magnification. Figure S9: SEM/EDX image of carbon felt. Figure S10: selected galvanostatic charge-discharge cycles at 15 mA cm⁻² in static mode for (a) 1.5 M HEDS+1.5 M K₂S₂, (b) 3 M HEDS, and (c) 3 M K₂S₂. Figure S11: cycling retention at 25 mA cm⁻² at SOC = 60% in (a) capacity and (b) coulombic efficiency. The cycling tests are in static mode. Figure S12: galvanostatic charge-discharge profiles of flow cell of (a) 0.5 M HEDS+0.5 M K₂S₂, (b) 1 M K₂S₂, and (c) 1 M HEDS at 20 mA cm⁻² at SOC = 60% at 70 mL min⁻¹. Figure S13: (a) cycling retention of 1.5 M HEDS+1.5 M K₂S₂ at 20 mA cm⁻² at flow mode (70 mL min⁻¹), (b) Selected galvanostatic charge-discharge profiles of S13a. Figure S14: capacity retention of 1.5 M HEDS+1.5 M K₂S₂ with CuS-coated graphite felt at 15 mA cm⁻² at static mode at SOC = 60%. Figure S15: (a) galvanostatic charge/discharge profiles of 1.5 M HEDS+1.5 M K₂S₂ with CuS-coated graphite felt at 5-25 mA cm⁻² at static mode. (b) Energy efficiency comparison at 5-25 mA cm⁻² between CuS-coated graphite felt and pretreated nickel foam at static mode. Figure S16: (a) capacity retention of 1.5 M HEDS+1.5 M K₂S₂ with CuS-coated graphite felt at 20 mA cm⁻² at flow mode (70 mL min⁻¹) at SOC = 60%. (b) Galvanostatic charge/discharge profiles of S16a.

Supplementary Materials

References


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