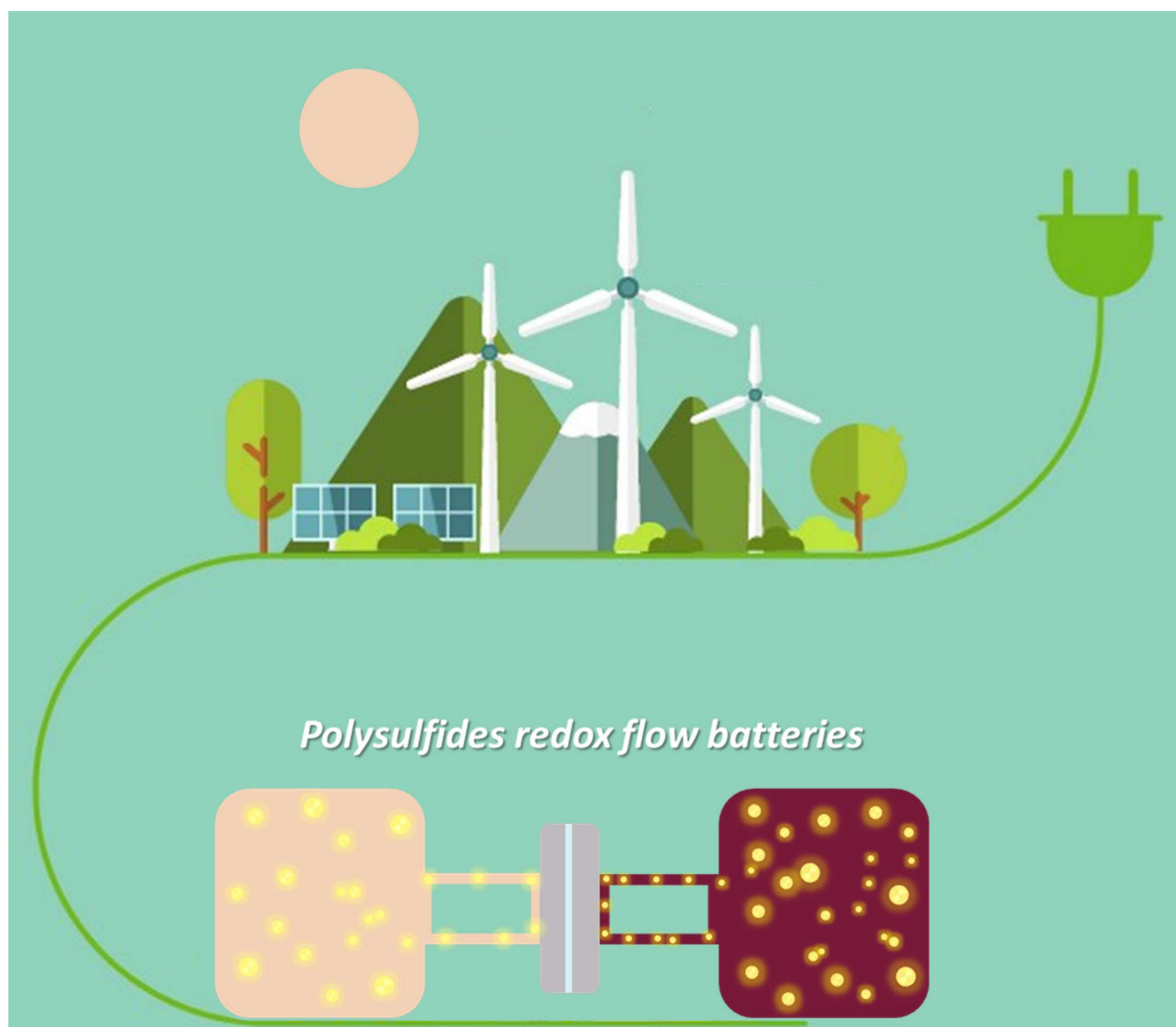


# Recent Progress in Polysulfide Redox-Flow Batteries

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Harvesting energy from intermittent and unstable renewable sources yet producing massive and stable output require large-scale energy storage systems. Redox-flow batteries have attracted extensive attention because of their flexibility and scalability and are promising large-scale energy storage systems for electrical grids. As an emerging member of the redox-flow battery family, polysulfide flow batteries exhibit a relatively high energy density with ultralow chemical cost of the redox active

materials. The special solution chemistry and complex conversions between sulfur and polysulfides with long and short chains lead to various system design schemes and complicated reaction mechanisms. Here, we present a review of various polysulfide flow battery systems developed to date and their underlying reaction mechanism and offer our perspective for their future development.

## 1. Introduction

More than 12% of worldwide electricity is now generated from renewable sources such as solar, wind, hydroelectric power and geothermal, and this percentage is expected to continue to grow rapidly.<sup>[1]</sup> For the power generation from the renewable sources, which are typically unstable and intermittent, to be smoothly integrated into electric grids, auxiliary energy storage systems are needed. Large-scale energy storage systems are being developed at a faster pace than ever before by the joint effort from the government and industry.<sup>[2]</sup> The United States Department of Energy (US-DOE) sets a short-term target cost of \$250/kWh and a long-term target of \$150/kWh for grid storage system<sup>[3]</sup> and emerging use-case studies suggest that the installed cost of <\$50/kWh is required for renewable energy generation to be economically competitive with fossil plants.<sup>[4]</sup> In order to meet these aggressive cost targets for large-scale commercialization of energy storage technologies, various electrochemical energy storage technologies, including flow and non-flowing secondary batteries,<sup>[5]</sup> rechargeable metal-air batteries,<sup>[6]</sup> regenerative fuel cells,<sup>[7]</sup> and supercapacitors,<sup>[8]</sup> are being investigated.<sup>[9]</sup> Each of these energy storage technologies has its advantages and most appropriate application area. For example, lead-acid batteries have relatively low cost, but suffer from limited energy density and environmental constraints.<sup>[10]</sup> Other types of battery, including nickel-cadmium, nickel-metal hydride and lithium-ion batteries have higher energy densities and longer cycle life, but cost-prohibitive as grid storage batteries.<sup>[11]</sup>

Among all the electrochemical technologies, redox-flow batteries (RFBs) are recognized as one of the most promising candidates due to their long service life, scalability, decoupled energy and power, easy maintenance and potentially low system cost.<sup>[12]</sup> These features of redox-flow batteries allow for wide ranges of discharge times and operational powers, making them ideal for providing various grid storage services. Typical all-liquid RFBs are operated based on the flow of anodic and cathodic electroactive redox solutions, which are stored in

external tanks and pumped through a reactor where redox reactions occur.<sup>[13]</sup>

The redox active solutions are composed of solvents and solutes. The solutes are organic or inorganic redox compounds while the solvents can be aqueous and nonaqueous.<sup>[13b,14]</sup> Recent developments in organic redox-flow batteries have been discussed by several review papers in great details.<sup>[12a,15]</sup> Sulfur is the 14<sup>th</sup> richest element in earth's crust and has the lowest cost per unit charge among available reactive materials.<sup>[16]</sup> Polysulfide redox species demonstrate excellent solubility in aqueous and organic solvents and have been widely used as the main reactants for sulfur-involved redox couples for RFBs.<sup>[5a,17]</sup> The high solubility is advantageous for polysulfide redox-flow batteries (PSRFBs) because the higher solubility of the active redox species, the higher the energy density of the batteries.<sup>[18]</sup> In this regard, PSRFBs systems based on polysulfide redox active materials could potentially decrease the chemical cost of redox couples with relatively high theoretical energy density to meet grid storage needs for renewable energy. For example, a low chemical cost of \$1/kWh was recently reported for a lab-scale hybrid aqueous polysulfides/air RFB, which opens a door toward achieving the ultralow system cost targets set by the US-DOE.<sup>[19]</sup>

This review focuses on PSRFBs and highlights the potential of polysulfide redox species in decreasing the chemical cost and increasing energy density. We will first give a detailed overview on the solution chemistry of polysulfides that often determines the energy density of PSRFBs. The solution chemistry of polysulfide redox species is governed by both their intrinsic properties and interactions with solvent molecules, and can greatly impact the system design and cell architecture.<sup>[20]</sup> Moreover, the reversible reaction process between different polysulfides ( $S_2^{2-}$ ,  $S_4^{2-}$ ,  $S_8^{2-}$ ,  $S_8^0$  and  $S^{2-}$ ) is further complicated by the existence of different cations, such as  $Li^+$ ,  $Na^+$  and  $K^+$ . This motivates us to provide a critical overview of the various PSRFBs from the perspective of polysulfide chemistry.

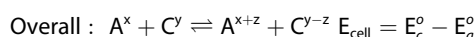
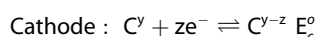
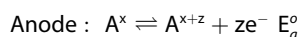
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## 2. Sulfur Chemistry of Polysulfide Redox-Flow Battery Systems

### 2.1. General Flow Battery System Architecture and Electrochemistry

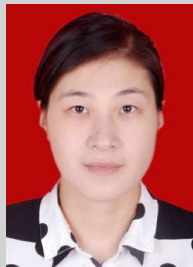
In PSRFBs, polysulfides undergo anodic or cathodic reversible reactions with the assistance of electrolytes to complete the energy conversion process. During the discharge and charge reactions, the cathodic and anodic electrolytes are pumped into the reactor for the half-cell reactions. The working principle of PSRFBs can be generally summarized as follows where polysulfide can be either A or C:



Different PSRFBs systems have been proposed and investigated. Table 1 summarizes the main types of PSRFBs under development. PSRFBs systems have two broad categories: all-liquid and hybrid systems. For all-liquid systems, the electroactive species are dissolved in solvents to make anolytes and catholytes, as schematically depicted in Figure 1a. Many organic solvents have been proven to have good solubility for polysulfides, such as DOL/DME, DMSO and THF, which are commonly used as solvents for polysulfides reactions.<sup>[21]</sup> The solution chemistry and potential window highly depends on the polysulfides' intrinsic properties and their interactions with solvent molecules.<sup>[22]</sup> Water can be used as solvent for PSRFBs which is low-cost but has limited electrochemical window, leading to possible water decomposition.<sup>[23]</sup> In addition to the hydrogen and oxygen evolution reactions (HER and OER) associated with the water decomposition, reactions between water and sulfur can also generate hydrosulfide ion ( $\text{HS}^-$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ) under certain pH conditions.<sup>[24]</sup> In contrast, organic electrolytes can possibly enable a wider



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Panni Zheng received her bachelor's degree in Mechanical Engineering from Virginia Tech. She is currently in the progress of Master's degree in Dr. Zheng Li's Lab. Her research interests focus on recycling of spent lithium-ion batteries (LIBs) and flow battery.



Fengchang Yang is currently a research & development engineer at JENSEN HUGHES, Inc. He obtained his PhD from Virginia Tech in 2017, and his past research focused on multiphysics modeling of complex systems involving fluid flow, heat and mass transfer, chemical reactions, etc. His research interest also includes safety science areas such as battery fire, solid material burning, pyrolysis of solid porous material.

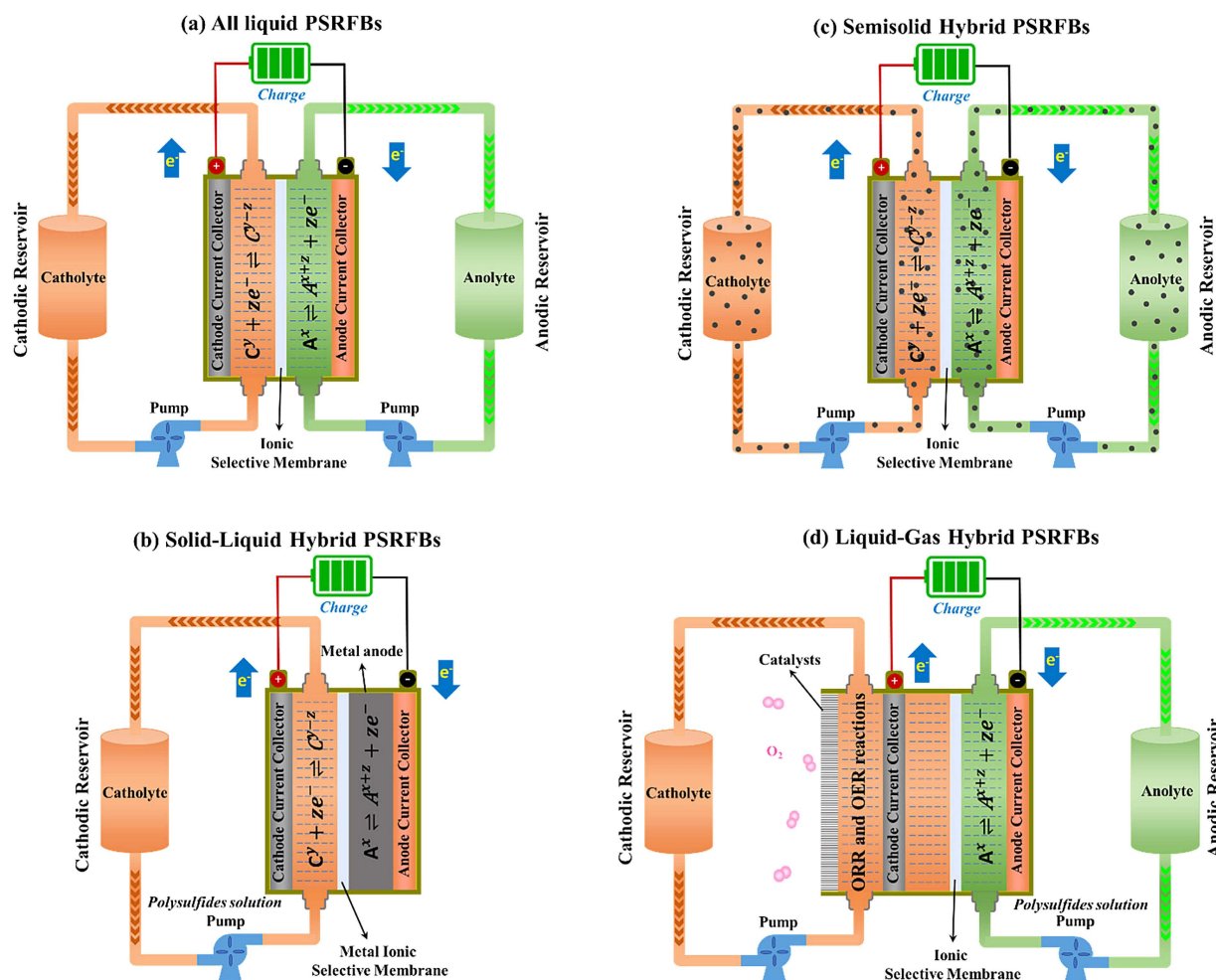


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Zheng Li is currently an assistant professor of Mechanical Engineering at Virginia Tech. His research interests center on the design, manufacturing and electrochemistry of energy storage systems. Dr. Li is a serial inventor in the energy storage field. He has led the prototype design of several game-changing battery technologies (e.g., aqueous sodium-ion battery, sulfur-based flow battery and lithium-ion battery recycling) at MIT and Virginia Tech. These inventions have resulted in 9 patent applications and 23 journal publications. Also, in pursuit of a great battery scientist, Dr. Li has gained rich industrial experience through research collaborations with scientists from various industry partners. He received his bachelor's degree in Materials Physics at Jilin University, Changchun in 2006 and his master's degree in Materials Science and Engineering at Tsinghua University, Beijing in 2008. He completed his Ph.D. in Materials Science and Engineering in 2011 at the State University of New York at Binghamton.

Systems	Electrodes	Examples	Negative electrolyte	Positive electrolyte	OCV (V)	Ref.
All-liquid PSRFBs	Aqueous	Polysulfide-Bromine	$\text{Na}_2\text{S}_x$	NaBr	1.3	[23a,25]
Hybrid PSRFBs	Solid-Liquid	Li-polysulfides (nonaqueous)	Li	Long-chain polysulfides	2.8	[26]
		Li-polysulfides (aqueous)	Li	Short-chain polysulfides	2.6	[27]
	Semi-Solid	Li/Na-S	Li/Na	S	2.5	[28]
	Liquid-Gas	Polysulfides-Air	Polysulfide	Air	1.5	[19]



**Figure 1.** Schematic representations of different system architectures of polysulfides redox-flow batteries: a) All-liquid PSFBs. b) Solid-liquid PSFBs with solid half-cell. c) Semi-solid PSFBs with semi-solid anolytes or catholytes. d) Liquid-gas PSFBs with an additional gas-liquid interface component.

operational potential window but with increased solvent cost, ionic resistivity and viscosity.<sup>[15c]</sup>

Hybrid PSRFBs can have three subcategories: solid/liquid, semisolid, and liquid/gas forms.<sup>[19,26a,27–28]</sup> A schematic of the solid/liquid form is shown in Figure 1b. Li or Na pure metal electrode is commonly used as the solid electrode. The system faces the problem of dendrite formation, which is also a major challenge for Li/Na metal batteries.<sup>[29]</sup> The liquid electrode features polysulfides dissolved in liquid solvents.<sup>[26a,27]</sup> While the energy density increases with increasing polysulfide concentration in the solvents, the energy efficiency decreases due to the higher flow resistance originating from the higher solution viscosities.<sup>[30]</sup> Reaction rates will decrease due to sluggish bulk

diffusion or less facile interfacial reaction rates. To circumvent these problems, some researchers turned to semisolid systems (Figure 1c) by utilizing conductive materials in polysulfide solution to enable highly distributed electrochemical reactivity throughout the electroactive zone of flow batteries.<sup>[28]</sup> The conductive materials in the solution (often carbon) can serve as a continuous nanoconductor network to facilitate the charge transfer and reduce the diffusion length between electroactive sites.<sup>[28b,31]</sup> Apart from the above electroactive redox couples and systems, a growing effort has been focused on developing novel flow battery systems to further decrease their cost and increase their energy density.<sup>[19,32]</sup> For example, as shown in Figure 1d, Li et al. recently reported a liquid/gas hybrid (Li/Na



polysulfides-air) PSRFBs using a half-cell reaction involving oxygen reduction (ORR) and evolution (OER) reactions.<sup>[19]</sup> In the following section, we will give a comprehensive overview of these different cell architectures along with their basic reaction mechanisms.

## 2.2. Polysulfide Solution Chemistry

The concentration of polysulfides in the electrolyte dominates the practical capacity and energy density of PSFBs. The solubility is closely related to the physicochemical properties of the solvent and polysulfide speciation, temperature, and the interactions between the polysulfides and a given solvent.<sup>[22,33]</sup> In general, sulfur is slightly soluble in many polar electrolyte solvents, while polysulfide chains with different chain lengths show different solubilities in aqueous or organic solvents, resulting in different conductivities, theoretical redox potentials and capacities (see, for example, the Li–S chemistry in Table 2).<sup>[24,34]</sup> In the aqueous electrolyte system, short-chain polysulfides ( $\text{Li}_2\text{S}_n$ ,  $1 \leq n < 4$ ) are usually used as redox active species for half-cell reactions with high conductivity but relatively low theoretical capacity.<sup>[24]</sup> The aqueous sulfur reaction pathway depends on the pH and sulfur concentration and electrolyte salt concentration of the aqueous electrolytes.<sup>[27]</sup> The high ionic conductivity of aqueous electrolytes significantly improves the sulfur utilization and the high solubility of short-chain polysulfide in the aqueous electrolyte avoid the precipitation issues of  $\text{Li}_2\text{S}$  in their organic counterparts. However, the intermediate sulfur species ( $\text{S}_n^{2-}$ ) tend to convert to  $\text{HS}^-$  and  $\text{OH}^-$  through an electrolyte hydrolysis.<sup>[35]</sup> Various studies involving the polysulfide host, electrolyte materials and cell design have been conducted in aqueous Li–S batteries to prevent the formation of  $\text{HS}^-$  or  $\text{H}_2\text{S}$ .<sup>[27,36]</sup> In addition, oxygen and hydrogen evolution reactions (HER and OER) during water decomposition are possible side reactions.<sup>[24]</sup> The redox potential of aqueous sulfur located between the pH dependent HER and OER would be crucial for the system stability. Increasing the electrochemical stability window of

aqueous electrolyte is desirable for the aqueous sulfur system.<sup>[36a]</sup>

On the other hand, the non-aqueous system requires long-chain polysulfides ( $\text{Li}_2\text{S}_n$ ,  $4 \leq n \leq 8$ ) species for conversion reactions between polysulfides. The redox chemistry of sulfur and their derivatives is complicated and challenging to control because of the many intermediate polysulfides species.<sup>[37]</sup> As shown in Table 3, polysulfides can be thermodynamically stable in solutions with various chain lengths ( $\text{S}_n^{2-}$ ,  $n = 2 \sim 8$ ).<sup>[37]</sup> For example, lithium polysulfides ( $\text{Li}_2\text{S}_n$  with  $n > 2$ ) can be easily synthesized through the reactions between sulfur and lithium sulfides.<sup>[38]</sup> However, the Gibbs free-energy of many polysulfides species are close to each other (see Table 3), indicating the possible co-existence of these anions in the solvents by a series of chemical equilibria.<sup>[34]</sup> The conversion reactions between polysulfide species affects the reaction reversibility, practical capacity, and long-term cycling performance. For most organic or aqueous electrolytes, the conversion reactions between the long-chain and short-chain polysulfides lead to the formation of undesirable insoluble intermediate polysulfides.<sup>[18a,39]</sup> Therefore, controlling the conversion reactions can greatly affect the electrochemical performance of PSRFBs. Sulfur substitutes such as sulfur-rich polymers have been recently developed to enhance the stability and reversibility of the electrochemical process in Li–S batteries.<sup>[40]</sup> This provides an alternative path on solving the aforementioned challenges for the aqueous and nonaqueous PSRFBs. In search of highly efficient sulfur catholyte, organic polysulfides (such as aliphatic, aromatic, heterocyclic and etc.), sulfur-rich compounds or polymers can be explored.<sup>[41]</sup>

The capacity and theoretical energy density are determined by the reactions between the  $\text{S}_2$ - $n$  species. Taking lithium-polysulfides flow batteries for example (Table 4), the practical energy density is determined by the utilized polysulfides conversion reactions and the concentration of the soluble polysulfides in the system.<sup>[21]</sup> Nonetheless, the concentration of polysulfides in the solution also affect the conversion reactions and the solubility of different polysulfides.<sup>[42]</sup> Designing half-cell reactions with optimized concentration of polysulfides is important for the achievable energy density, rate and cycling

**Table 2.** The comparison of key properties of polysulfide solution by taking an example of aqueous and organic Li–S chemistries.<sup>[24]</sup>

	Organic solutions	Aqueous solutions
Solubility	Sulfur (Low) Long-chain polysulfides (High) Short-chain polysulfides (Low)	Sulfur (Low) Long-chain polysulfides (Low) Short-chain polysulfides (High)
Ionic conductivity of electrolyte	0.2–35 mS/cm	~ 127 mS/cm
Voltage	Reduction: 2.30/2.05 V vs $\text{Li/Li}^+$ Oxidation: 2.4 V vs $\text{Li/Li}^+$	Reduction: –0.38 V vs SHE (2.62 V vs $\text{Li/Li}^+$ ) Oxidation: –0.7 V vs SHE (2.30 V vs $\text{Li/Li}^+$ )

**Table 3.** Thermodynamic data of various polysulfides anions ( $\text{S}_2$ - $n$ ) formed in aqueous solutions.<sup>[34]</sup>

	$\text{S}_2^{2-}$	$\text{S}_3^{2-}$	$\text{S}_4^{2-}$	$\text{S}_5^{2-}$	$\text{S}_6^{2-}$	$\text{S}_7^{2-}$	$\text{S}_8^{2-}$
$\Delta G^\circ$ , kJ/mol	$77.4 \pm 1.3$	$71.1 \pm 0.7$	$67.1 \pm 0.1$	$66.0 \pm 0.1$	$67.4 \pm 0.1$	$70.7 \pm 0.3$	$74.9 \pm 0.5$
$\Delta H^\circ$ , kJ/mol	13.0	$6.6 \pm 0.1$	$9.0 \pm 0.1$	$9.6 \pm 0.1$	$13.3 \pm 0.1$	$16.5 \pm 0.1$	$23.8 \pm 0.2$
$S^\circ$ , kJ/mol	–22	$9 \pm 4$	$63 \pm 1$	$100 \pm 2$	$139 \pm 1$	$171 \pm 4$	$213 \pm 8$

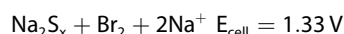
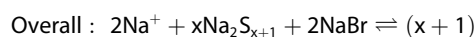
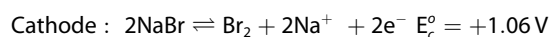
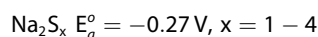
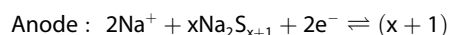
**Table 4.** Calculation of the energy density of Li–S flow batteries with different sulfur concentration.<sup>[21]</sup>

		$S_8^{2-} \rightarrow S_4^{2-}$	$S_8^{2-} \rightarrow S_2^{2-}$	$S_8^0 \rightarrow S_4^{2-}$	$S_8^0 \rightarrow S_2^{2-}$	$S_8^0 \rightarrow S^{2-}$
Capacity (mAh/g)		209	627	418	836	1672
Voltage (V)		2.2	2	2.2	2	2
Energy density (Wh/kg)		459	1254	919	1672	3344
Volumetric energy density (Wh/L)	0.5 M	7	20	14	26	53
	1 M	14	40	29	53	106
	2 M	29	80	58	107	213
	5 M	13	125	147	214	534
	10 M	146	250	294	428	1068

performance. So far, few fundamental studies have been reported on how to control the conversion reactions between polysulfides in electrolytes, which is critical for enabling long-life PSRFBs and their large-scale applications.

### 2.3. Aqueous Polysulfide Flow Batteries

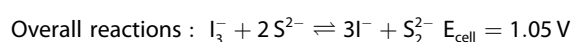
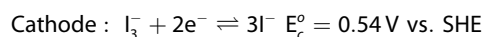
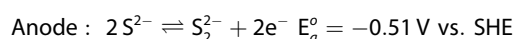
A bromine-polysulfide flow battery was first reported by Remick et al. in 1983<sup>[23a]</sup> and later by the Regenesys Ltd.<sup>[43]</sup> The anolyte is a polysulfide/sulfide aqueous solution, while the bromine/bromide, chlorine/chloride, or iodine/iodide solution serves as the catholyte. Na-ion conducting Nafion membranes were used to separate of the two half-cells. During the discharge, short-chain polysulfides and sulfides solution is pumped into the anodic half-cell to be oxidized to high-chain polysulfides, as shown in the following reactions. For the cathode reactions, bromine is reduced to bromide with the charge compensation by the  $Na^+$  ion.



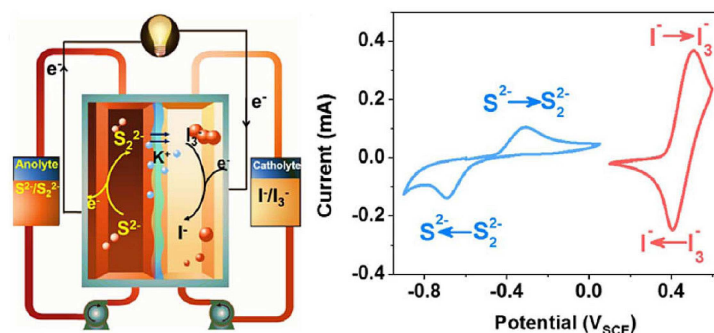
To alleviate the issue of the sluggish polysulfide/sulfide reaction kinetics, carbon electrodes were coated with nickel or cobalt. The metal-coated carbon felt electrodes demonstrate

better performance than their un-coated counterparts.<sup>[44]</sup> However, the metal-coated carbon electrode only shows improved electrochemical performance in the initial short-term cycles with an energy efficiency over 80% at 40 mA/cm<sup>2</sup>. After about 50 cycles, an obvious capacity decay is observed. The main reason for this performance degradation is the over-accumulation of sulfur in the metal-coated carbon felt electrodes. The conversion reactions between the polysulfides, sulfides and sulfur are difficult to control in many systems, such as Li–S batteries. The irreversible conversion reactions forming elemental sulfur induce the capacity loss and elevated mass transport resistance. In addition to the sulfur over-accumulation on carbon electrodes, bromine is volatile and toxic, which is challenging for building large-scale PSRFB systems.<sup>[45]</sup>

Recently, several research groups reported polysulfide/iodide flow batteries.<sup>[25,46]</sup> In Figure 2, the KI and  $K_2S_2$  with high solubility are used as the redox active materials in the catholytes and anolytes, respectively. Based on the following working principle, the theoretical energy density is estimated to be as high as ~85.4 Wh/L.



In the lab prototype, the all-liquid PSRFBs demonstrated an energy density of ~43.1 Wh/L with a low chemical cost of \$85.4 kW/h. By using 4 M KI–3M  $K_2S_2$ , the batteries can maintain a stable performance with a high Coulomb efficiency of 97%

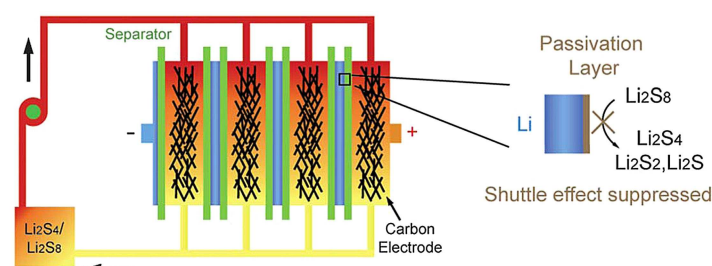


**Figure 2.** A schematic illustration of the aqueous polysulfide/iodide redox-flow batteries (left) and the cyclic voltammograms (right) of 5 mM  $K_2S_2$ –0.5 M KCl solution (blue) and 5 mM KI–0.5 M KCl solution (red) on a gold electrode.<sup>[25]</sup>

under the current density of  $15 \text{ mA/cm}^2$  during the initial 50 cycles. The system shows an enhanced performance for the aqueous PSRFBs system. The average voltage plateau is found to be only  $\sim 0.9 \text{ V}$  and overcharge phenomenon can be observed from the initial first cycle, indicating the existence of side reactions in this system. The water decomposition reaction may be the main reason, which would further impact the pH value and long-term performance. Therefore, the aqueous system of PSRFBs still face critical issues of stable cycles and the control of polysulfides reactions.

## 2.4. Solid-Liquid Hybrid PSRFBs

Taking advantage of the high energy density of lithium metal anode and the scalable architecture of the flow batteries,<sup>[31,47]</sup> the lithium-polysulfides redox-flow batteries are promising candidate for large-scale energy storage applications due to the low chemical cost and high solubility of polysulfide species. In lithium-polysulfides system, the long-chain polysulfides species are often dissolved in organic solvents (e.g., DOL/DME, THF and DMSO) to form catholytes.<sup>[21]</sup> However, in this system, the precipitation of short-chain lithium sulfide usually leads to the loss of active materials and capacity decay during the long-term cycling.<sup>[39,48]</sup> Cui's group reported a membrane-free hybrid PSRFBs with long-chain polysulfides in non-aqueous solvent as catholyte and lithium metal as anode, as shown in Figure 3.<sup>[26a]</sup> By controlling the cycle reaction between  $\text{Li}_2\text{S}_8$  and  $\text{Li}_2\text{S}_4$ , the two-electron reaction, through using narrow voltage window, avoids the precipitation issues related to  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  short-chain polysulfides. This system demonstrated a high energy density of  $97 \text{ Wh/kg}$  and  $108 \text{ Wh/L}$ . As the lithium anode is well passivated by  $\text{LiNO}_3$  additive in the electrolyte, the shuttle effect associated with polysulfides is alleviated. The cells with low concentration of polysulfides showed stable cycling of more than 200 cycles, while the cells with higher polysulfide concentrations showed obvious capacity fade. Introducing nanoscale conductor networks in the system enables the deep cycling of polysulfide solutions into precipitation regimes, further improving the capacity utilization and cycling performance.<sup>[28b]</sup> Alternatively, separator membranes design that alleviates polysulfide crossover on the Li anode surface can significantly improve battery performance even in the absence of  $\text{LiNO}_3$  anode-protecting additives.<sup>[49]</sup>

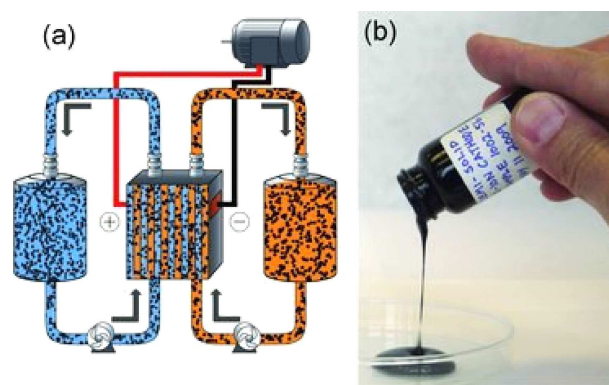


**Figure 3.** The schematic of a Li-polysulfides flow batteries with lithium polysulfide ( $\text{Li}_2\text{S}_8$ ) in ether solvent as the catholyte and metallic lithium as the anode.<sup>[26a]</sup>

An aqueous system was developed by using short-chain lithium polysulfides as the redox active species.<sup>[27,50]</sup> To protect the lithium metallic anode from contacting aqueous catholyte, the LISICON ceramic membrane  $\text{Li}_{1.35}\text{Ti}_{1.75}\text{Al}_{0.25}\text{P}_{2.7}\text{Si}_{0.3}\text{O}_{12}$  (LATP) was used. Taking advantage of the high solubility of short-chain lithium sulfides ( $\text{Li}_2\text{S}_4\text{--Li}_2\text{S}$ ) in aqueous solution ( $> 5 \text{ M}$ ), the demonstrated cell has a high energy density of  $387 \text{ Wh/L}$ .<sup>[51]</sup> The application of LATP solid-state electrolytes suppresses the polysulfides shuttle effect. However, LATP is not stable in direct contact with metallic Li anode and therefore multiple layers of solid electrolytes or liquid electrolyte are often needed to stabilize the interface.<sup>[52]</sup> Although solid anode materials possess higher energy density than liquid anolytes, the dendrite formation of alkali metal anode is a critical challenge for large-scale applications.<sup>[53]</sup> Solid-state electrolyte can, to some extent, prevent the lithium dendrite, but still face unstable issues during long-term cycling.<sup>[54]</sup>

## 2.5. Semisolid Hybrid PSRFBs

The concept of semisolid flow batteries was first proposed by Chiang and co-workers by using a flowable suspension of redox-active materials as flow battery electrodes (Figure 4).<sup>[31,55]</sup> Using redox-active materials suspension instead of solution dramatically increases the energy density of the flow batteries



**Figure 4.** a) A semisolid flow cell. b) Demonstration of the flowability of a semisolid suspension containing  $\text{LiCoO}_2$  powder (active material) and Ketjen black (dispersed conductive phase) and the alkyl carbonate electrolyte.<sup>[31]</sup>

and utilizes the capacity of the redox active species beyond their solubility limit in the solutions.<sup>[56]</sup> Chiang et al. reported the semisolid electrodes composed of solid active Li-ion materials, such as  $\text{LiFePO}_4$ ,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  or  $\text{LiCoO}_2$ , suspending in electrolyte solutions.<sup>[31]</sup> The semisolid concept was also applied to the PSRFBs by introducing conductive nanomaterials into the polysulfides solution to improve the reaction rate of polysulfide redox species. Chiang's group reported a non-aqueous PSRFBs where nanoscale conductive particles were mixed with polysulfide solutions to form a flowable electrode with embedded current collector networks.<sup>[28b]</sup> The polysulfide catholyte demonstrate higher electrochemical activity, mainly attributable to the percolating conductive network serving as the additional current collectors. A high reversible capacity of 600 mAh/g was achieved at an average voltage of 1.9 V. However, only 56% capacity retention after 100 cycles was observed when cycling the polysulfide suspension between 2.55–2.00 V in Li/Polysulfide suspension cell. When cycling between 1.90–2.50 V to include  $\text{Li}_2\text{S}$  precipitation region, a high initial specific capacity of 1200 mAh/g was achieved but faster capacity decay was observed with only 610 mAh/g after 100 cycles. Better catholyte design for higher efficiency and cycle life is still needed. Overall, the semisolid system provides a promising solution on achieving low cost PSRFBs. The materials cost of the suspension catholyte is calculated to be as low as ~\$21/kWh and the redox couple materials is ~\$37/kWh assuming 100% excess of the Li metal.

Recently, Li's group reported a semisolid hybrid Na–S flow battery by utilizing molten sodium metal as anode,  $\beta''\text{-Al}_2\text{O}_3$  as membrane, and flowable sulfur-based suspension as catholyte (Figure 5).<sup>[28a]</sup> Different from the existing high-temperature Na–S batteries, this flow battery decouples the thermal management systems by controlling different operation temperature for the power stack and the storage tank.<sup>[57]</sup> To enhance the conductivity of the catholyte and facilitate the redox reactions, 2 vol% Ketjen and 1 M NaI were added into

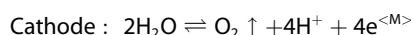
the TEGDME solution. At low discharge current density, a high storage capacity of ~864 mAh/g was obtained, which is much higher than that of the traditional high temperature Na–S batteries. When cycling the Na–S flow battery at 150 °C at a current density of 0.5 mA between 1 and 2.5 V, the reversible capacity reach to 705 mAh/g in the first cycle but show fast capacity decay to ~484 mAh/g after 55 cycles. More investigation on the capacity decay are needed to reveal the reaction mechanism in the intermediate temperature Na–S flow system. The system cost is estimated to be in the range of 50–100 \$/kWh, which is very promising to achieve cost target set by DOE.<sup>[3]</sup>

## 2.6. Liquid-Gas Hybrid PSRFBs

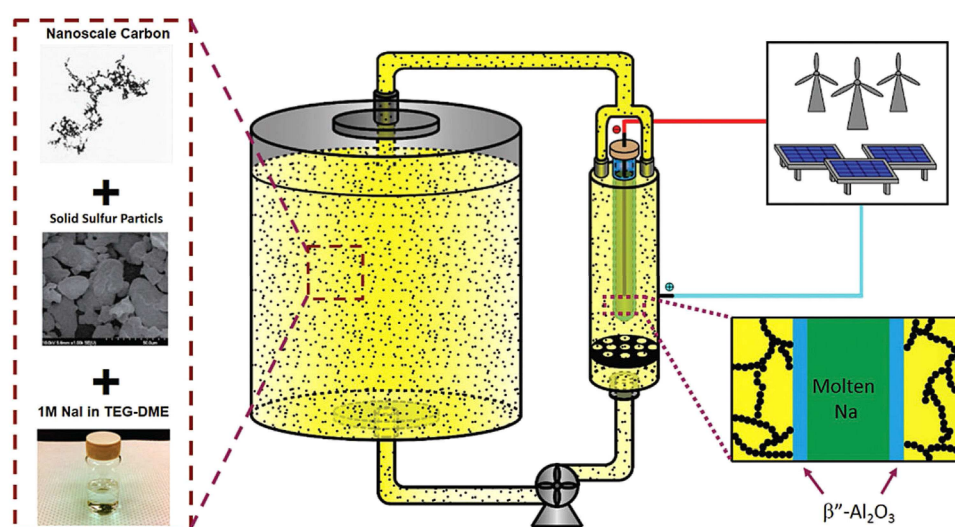
Inspired by the fuel cell chemistry, a vanadium-air RFB was proposed in order to further decrease the weight and size of the flow batteries in 1994.<sup>[58]</sup> By utilizing 1.2 M  $\text{V}_2(\text{SO}_4)_3$  in 2 M  $\text{H}_2\text{SO}_4$  as the anolyte and a bifunctional cathode with  $\text{IrO}_2$ -based catalyst, the cell showed a low energy efficiency of only 41.6% and poor cycle life. The low efficiency and fast capacity decay are mainly due to the loss of active materials, the current collector corrosion, and the crossover effect.<sup>[59]</sup>

Recently, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) were also introduced into aqueous sulfur systems.<sup>[19]</sup> The polysulfides and oxygenated/aerated salt solutions were used as the anolyte and catholyte, respectively (Figure 6). By using the Li/Na-ion conductive Li/Na-SICON as the membrane to separate the anolyte and catholyte, the batteries provide a theoretical cell voltage of 1.68 V or 0.85 V.

Acidic catholyte:

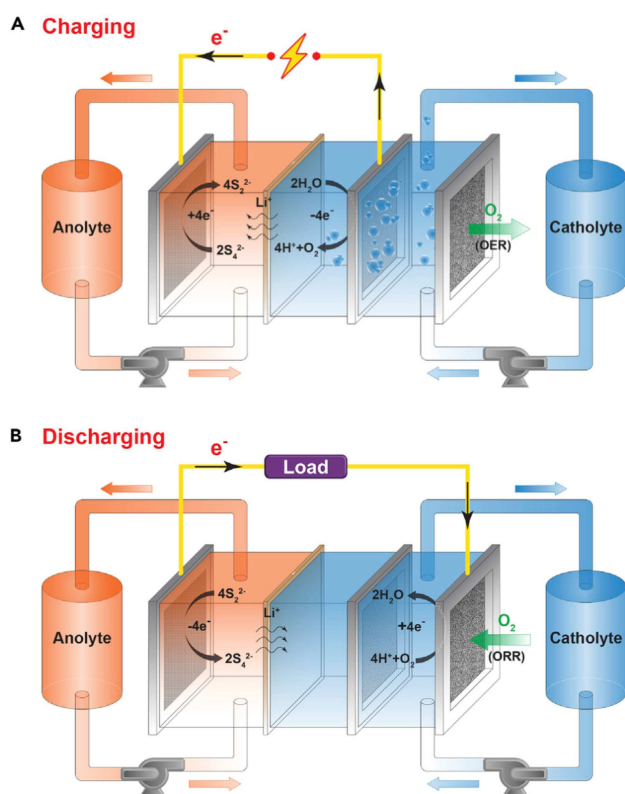


$$E_c^\circ = 1.299 \text{ V vs. SHE}$$



**Figure 5.** Semi-solid Na–S flow battery. Molten sodium metal as anode,  $\beta''\text{-Al}_2\text{O}_3$  as membrane and sulfur particles, 2 vol% Ketjen carbon and 1 M NaI in TEGDME as catholyte.<sup>[28a]</sup>





**Figure 6.** Liquid-gas hybrid PSRFBs by applying aqueous polysulfide solution as the anolyte and acidic or alkaline solution as the catholyte.<sup>[19]</sup>

Anode :  $xS_y^{2-} + 2(y-x)e^- \rightleftharpoons yS_x^{2-}$   $E_a^\circ = -0.447 \text{ V vs. SHE}$

Alkaline catholyte:

Cathode :  $4OH^- \rightleftharpoons O_2 \uparrow + 2H_2O + 4e^-$

$E_c^\circ = 0.401 \text{ V vs. SHE}$

Anode :  $xS_y^{2-} + 2(y-x)e^- \rightleftharpoons yS_x^{2-}$   $E_a^\circ = -0.447 \text{ V vs. SHE}$

Although the cathodic potential is higher in the acidic system than that of the alkaline electrolyte, the acidic electrolyte needs high-cost catalysts (e.g., precious metals). Controlling the concentration of polysulfides in the cathodic solution, the hybrid PSRFBs could demonstrated an energy density in the range of 30–145 Wh/L. Meanwhile, the chemical cost of the active materials in the system is ultra-low per stored energy, estimated to be ~\$1/kWh when using sodium polysulfide as the cathodic redox active materials.

For liquid-gas hybrid system, noble-metal catalysts are often used in the cathode for the oxygen evolution/reduction reactions which generally increases the overall cost of the system.<sup>[60]</sup> Considering the low efficiency of the ORR and OER process, more research is needed to introduce oxygen chemistry into flow battery systems.<sup>[61]</sup>

### 3. Conclusions and Outlook

Redox-flow batteries based on polysulfide species show great potential for large-scale energy storage in grid applications. In this review, we have discussed various PSRFBs that utilize sulfur-containing redox active catholyte or anolyte. Compared with the conventional all-liquid flow battery system, the hybrid systems including solid-liquid, semi-solid and liquid-gas system, can potentially increase the system energy density and lower the cost by using suspension or metal electrode. Meanwhile, hybrid flow battery systems also have new design challenges due to the introduction of new forms of the reactants. For the electrochemical performance, the reversibility, long-term stability, and integration of inexpensive components (including redox couples, ion-selective membranes and solvent) in PSRFB systems still need fundamental understanding and further development. We suggest that the future research should focus on the following materials, reactions mechanism, and system design issues:

(1) For the polysulfide conversion reactions, detailed reaction mechanism between sulfur, disulfides, short-chain and long-chain polysulfides requires further investigation and how to control the reaction pathway of these complex reactions in a specific electrolyte should be explored. Developing sulfur substitute, such as sulfur-rich polymers or organic polysulfides, may offer alternative ways to optimize and improve the cycle life of PSRFBs.

(2) The stability and cost of solid-state electrolyte or ion-exchange membrane should be taken into design consideration. The solid-state electrolyte in the hybrid PSRFBs system still have issues on chemical and mechanical stability, low ionic conductivity, and high cost. The ion-exchange membranes also need improvement to prevent the cross-over effect in all-liquid PSRFBs. Therefore, we still have to explore ion-selective and cost-effective membranes with high conductivity and long service lifetime.

(3) New electrochemical redox species for PSRFBs based on low-cost, safe and highly soluble components should be further explored to achieve improved reversibility and system architecture.

(4) Redox mediators or soluble catalysts for PSRFBs should be explored. These materials can improve the reactions kinetics for the multi-electron transfer reactions in PSRFBs. In addition, redox mediators can effectively increase the practical energy density with enclosed configurations, which has been developed for other flow battery systems but rarely reported for PSRFBs.<sup>[62]</sup>

(5) PSRFBs are one of the most promising candidates for large-scale energy storage technologies for electric grid. The reversibility, long-term stability and integration of inexpensive components (including redox couples, ion-selective membranes and solvent) in PSRFB systems still need further development.

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## Conflict of Interest

The authors declare no conflict of interest.

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