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Review

Halogen Hybrid Flow Batteries Advances for Stationary Chemical Power Sources Technologies

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Abstract: This review aims to highlight the current advances in hybrid redox flow battery (HRFB) technology, encompassing one of the best combinations of efficiency, cost and flexibility due to its module construction, which offers independent scaling of power density and energy capacity. This work emphasizes the interest of the scientific community both in (i) studying the properties and principles of HRFB operation in order to improve commonly proposed systems, and in (ii) the development of energy storage devices with new reagent types or RFB concepts. The data provided enhances the reader to conclude whether novel concepts in halogen oxidizers utilization could help to overcome the problem of insufficient power and energy densities of common RFB.

Keywords: hybrid flow batteries; zinc-bromine flow batteries; hydrogen-bromate flow batteries; halogen electrolytes

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1. Introduction

The well-known 17 Sustainable Development Goals (SDGs) are at the hearing today to form the 2030 ecological agenda majors [1]. Among them, the reliable technologies to provide energy in a sustainable way are limited by insufficient usage of renewable energy sources. Due to the intermittent availability of the latter, the demand for effective energy storage systems (ESS) today is of crucial importance.

The distributed energy resources (DER) model is another ace in the hole that offers more flexible and integrative energy storage mechanisms within the local power grid close to the end user, thus minimizing the demand for power transmission lines usage [2]. An essential solution to the problem of energy accumulation and storage in distributed networks is the use of chemical power sources (CPS). Among the most effective energy systems for stationary applications, a special place is occupied by redox flow battery (RFB) technology, encompassing easy scalability with independent scaling of power density and energy capacity, no detrimental effects of a deep discharge, very low self-discharge, low cost for a large system compared to other types of batteries, and long cycle life [3].

However, the wide distribution and commercialization of flow batteries are currently hindered by their insufficient energy capacity and power, primarily due to the low energy density of reagents used [4]. To achieve significant capacity, the electrolyte tanks have to be large enough, along with the aqueous electrolyte, which often makes the battery very heavy and suitable only for stationary applications. Hybrid flow batteries (e.g., zinc-bromine, zinc-cerium, zinc-iron, iron-iron), which have a liquid-solid electrochemical reaction, are prone to additional degradation due to dendrite formation and increased resistance, while the common all-liquid systems such as vanadium and polysulfide bromide often require

electrolyte conditioning, a process of balancing the electrolyte chemistry using additional hardware or maintenance steps, which is required daily.

The high application potential of RFB ensures continued interest of the scientific community both in (i) studying the properties and principles of their operation to improve commonly proposed systems, and in (ii) the development of energy storage devices with new reagent types or RFB concepts. These modern studies of RFB are primarily aimed at overcoming two fundamental barriers that significantly hinder the development of the direction: (a) insufficient specific power due to small values of exchange currents for heterogeneous redox reactions used in RFB and (b) low energy density compared to the competing CPS, due to insufficient energy capacity of the reagents per unit volume or mass. To solve these issues scientific community proposed a number of concepts, such as the use of hybrid systems, in which one of the half-reactions in the battery is either replaced by a hydrogen oxidation reaction [5–8] or an electroactive component in a solid state [9–11]. In novel fundamental concepts, high-capacity electrolytes are proposed either in specific states, e.g., [8,12–14] or in specific forms, e.g., various salts of halates as highly soluble multielectron redox-active components [15]. This work aims to highlight recent advances in the hybrid redox flow batteries (HRFB) field and conclude whether novel concepts in halogen oxidizers utilization could help to overcome the problem of insufficient power density and energy capacity of RFB.

2. The Main Energy Storage Technologies Analysis

This work among other goals presents a staggered analysis of the main energy storage technologies, that compares specific power density and energy capacity of the system and technological parameters, such as system service life and cyclability. One of the common ways to compare different technologies in terms of the specific power density (W kg^{-1}) vs. the specific energy density (W h kg^{-1}) is the so-called Ragone diagram, first proposed in [16] (see Figure 1 and Table 1).

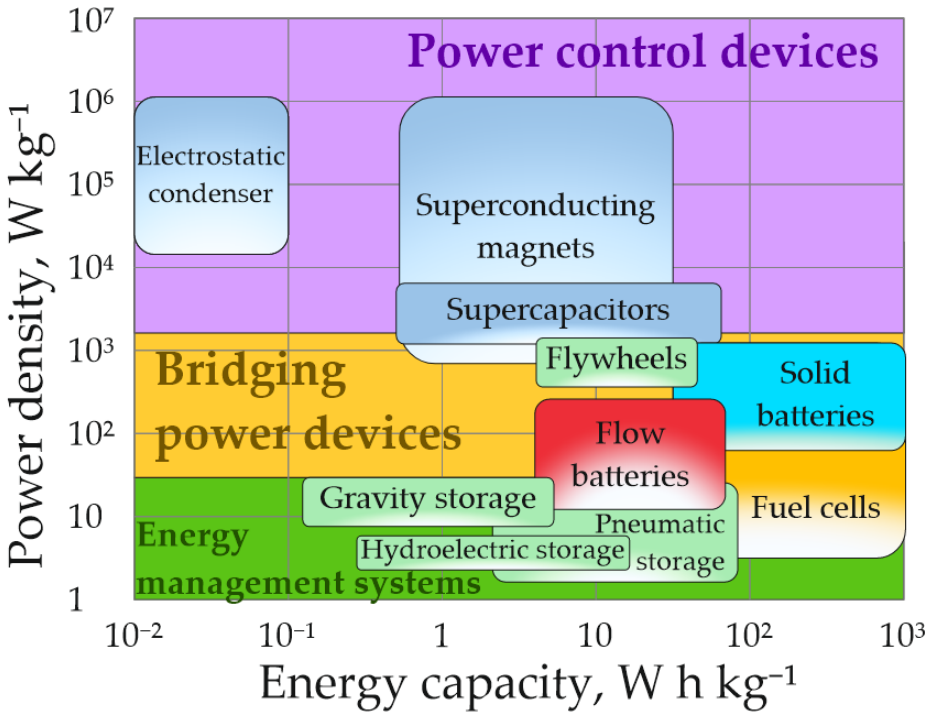

Figure 1. Dependence of specific power density vs. energy density (Ragone diagram) for the main electrical energy accumulation and storage technologies.

Table 1. Specific energy and power densities for the main electrical energy accumulation and storage technologies.

Power Source Operating Principle	Gravimetric Energy Density, W h kg^{-1}	Specific Power Density, W kg^{-1}	Source
Electrostatic capacitor	0.01–0.1	$1{\cdot}10^4$–$1{\cdot}10^6$	[17]
Supercapacitor	1–75	$1{\cdot}10^3$–$1.4{\cdot}10^3$	[17,18]
Superconducting magnet	0.5–30	$5{\cdot}10^2$–$1{\cdot}10^6$	[19,20]
Gravity storage	0.1–0.5	0.5–1.5	[21,22]
Hydroelectric storage	0.2–0.5	0.5–5	[19,23]
Pneumatic accumulator	3–60	2–24	[24,25]
Flywheel	10–30	400–1500	[19,26,27]
Lead acid battery	33–42	80–300	[19,25,28]
Nickel-cadmium battery	50–75	150–500	[19,24,25,28]
Nickel-metal hydride battery	60–70	200–1500	[24,25,28]
Sodium sulfur battery	150–240	150–250	[19,24,25]
Nickel salt battery	100–125	150–200	[19,24,25,28]
Li-ion battery	75–265	80–250	[19,25,28–30]
Fuel cell with proton exchange membrane	300–1000	4–675	[19,24,25,31]
Methanol fuel cell	140–960	2–20	[25,32]
Fuel cell based on molten carbonate	100–610	8–36	[25,33]
Solid oxide fuel cell	410–1500	10–80	[25,33]
Vanadium flow battery	10–50	30–170	[19,25,34]
Iron-chromium flow battery	5–25	22–116	[34]
Polysulfide-bromine flow battery	10–45	5–28	[8,35–37]
Iron-titanium redox flow battery	10–50	14–74	[38]
Organic flow redox battery	10–40	1–100	[39]

The diagram clearly demonstrates three functional groups for the main electrical energy accumulation and storage technologies:

Power control devices are designed to ensure a smooth power supply and maintain the electric power quality, requiring prominent specific and peak power (up to 1 MW) and rapid response (from several milliseconds to one second) to the changes in power grid operation regime at relatively weak energy capacity requirements for a complete discharge of the system up to several minutes.

Bridging power devices are used to maintain the voltage in the network while switching power-generating devices. They provide total power in the range from 1 kW to 10 MW (specific power from 10 W kg^{-1}) and energy capacity enough to perform the complete discharge in about 1 h (specific energy consumption in the range of 10 W h kg^{-1} and above) with the time order of seconds to enter the operating mode under load.

Energy management devices are used to replace the main power generators for long-term energy storage with a power limit from 1 kW to tens and hundreds of MW, designed for complete discharge over a period of several hours to days, with relatively weak requirements for peak and specific power and the time order of one hour to enter the operating mode under load.

Based on Figure 1 one can conclude that (1) capacitors, supercapacitors and superconducting magnets, as well as flywheels and gyroscopes, are best suited as devices for ensuring the quality of electricity in the network and smooth power supply to electrical consumers; (2) power sources operating on the principle of galvanic cells suit well for maintaining voltage in the power grid when switching between different power supply systems; (3) The requirements for devices for stationary energy storage are met by gravity energy storage devices, hydroelectric storage, and devices that store energy in the compressed air form. The design of redox flow batteries implementing independent scaling of energy capacity and power together with an exemplary combination of efficiency and cost allows them to use both in bridging power and energy management devices.

For stationary energy storage applications, in addition to the requirements for specific energy capacity and power, the scalability of the technology as well as its durability

plays a significant role. According to Table 1 majority of modern chemical power sources (secondary power sources operating on the principle of galvanic cells, fuel cells and flow batteries) satisfy the minimum requirements for energy storage devices in terms of specific energy capacity and power. Nevertheless, the scaling requirements for power systems and their reliability during operation impose significant additional restrictions on the choice of technology.

Table 2 and Figure 2 present the results of the existing technologies comparison in terms of technological parameters–average efficiency, total energy capacity for real system prototypes, characteristic energy storage time intervals, and average service life. Technologies without existing commercial prototypes were not included for comparison.

Table 2. Comparison of scalability, reliability and efficiency of the main electrical energy accumulation and storage technologies.

Power Source Operating Principle	Average System Efficiency, %	Total Energy Capacity [1], MW h	Characteristic Energy Storage Times, Sec–Months	Average Service Life, Years (Number of Cycles)	Source
Gravity storage	70–80	0.1–3	1–24 h and more	50	[22]
Hydroelectric storage	70–87	100–3000	1–24 h and more	30–60	[40–42]
Pneumatic storage	70–89	50–300	1–24 h and more	20–40	[19,42–44]
Flywheel	70–90	1–20	Less than 15 min	15–20	[19,42,45]
Lead-acid battery	80–90	$1 \cdot 10^{-5}$–10	sec–days	5–10 (200–1000)	[42,46,47]
Nickel-cadmium battery	60–80	$1 \cdot 10^{-5}$–30	sec–hours	10–15 (500–2500)	[42,48]
Nickel-metal hydride battery	65–90	$1 \cdot 10^{-5}$–5	sec–hours	10–15 (1000–1800)	[49,50]
Sodium-sulfur battery	75–90	$1 \cdot 10^{-5}$–5	sec–up to 10 h	5–15 (2500–5000)	[51–55]
Nickel-salt battery	75–90	$1 \cdot 10^{-5}$–5	sec–hours	5–15 (2500–4500)	[56–58]
Lithium-ion battery	75–92	$1 \cdot 10^{-5}$–10	sec–days	5–15 (2000–5000)	[19,59–61]
Fuel cell with proton exchange membrane	20–85	$1 \cdot 10^{-5}$–2	sec–months	1–3	[62–64]
Molten carbonate fuel cell	70–80	1–100	min–months	5–10	[65–68]
Solid oxide fuel cell	60–85	$1 \cdot 10^{-5}$–1	min–days	2–5	[68–72]
Vanadium flow battery	65–85	$1 \cdot 10^{-5}$–200	sec–months	10–20 (10,000)	[73,74]
Iron-chromium flow battery	70–80	$1 \cdot 10^{-5}$–100	sec–months	10–20	[34,75–77]
Polysulfide-bromine flow battery	70–80	$1 \cdot 10^{-5}$–12	sec–months	5–15	[8,78–81]

[1] For prototype systems put into operation.

The cost of power and energy indicators play an important role in the accumulation and storage technologies development. In general cases, the cost of power measured in currency units ($ US) per kW^{-1} means the price for generating one kW of energy considering the price contribution of fabricating all consisting components and assembly of the corresponding energy storage devices without considering expenditures on its maintenance. The cost of energy, measured in currency units per kW^{-1} h^{-1} represents a similar value, but for storing one kW h. These indicators strongly depend on the total energy capacity of the electric storage device: the better technology lends itself to scaling, the smaller will be difference in price per kW or kW h for an electric storage device with a total energy capacity and power on the kW or MW scale. Therefore, in Table 3 cost indicators are given as intervals, where a larger cost corresponds to a larger scale [82–87].

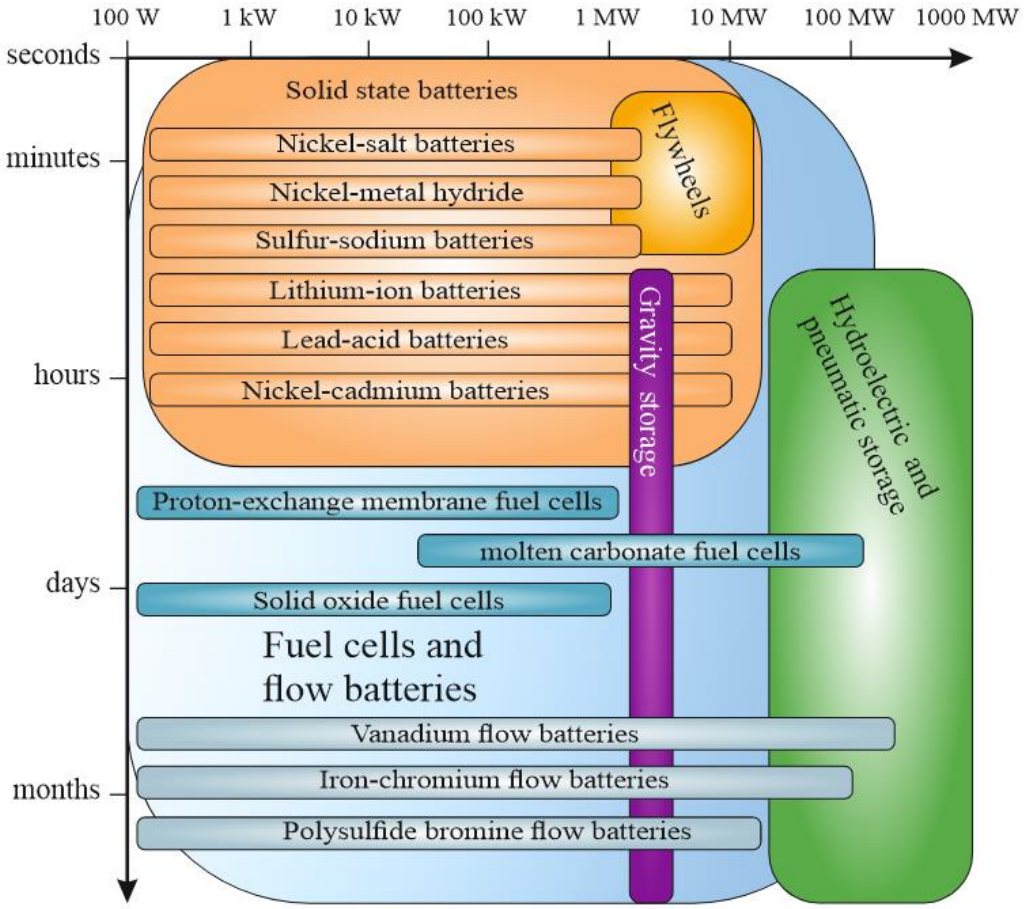

Figure 2. Characteristic scales in terms of storage time and volume of stored energy for the main electrical energy accumulation and storage technologies.

This preliminary analysis shows several promising energy storage technologies favorable for distributed energy applications, all of them fiercely ousting the traditional energy sources in terms of cost, processability, environmental friendliness and efficiency. Based on this data applicability limits can be determined for each of the currently existing energy storage systems. Thus, in the range from hundreds of kW to hundreds of MW, flow batteries have several significant advantages over competing technologies: long service life, stable cycling performance and the possibility of deep discharge without consequences, structurally independent scaling of power density and energy capacity, the absence of self-discharge and the chemical stability of the reagents. Therefore, they can serve both as bridging power and energy management devices.

Today a necessary condition for increasing the commercial attractiveness of redox flow batteries is the creation of chemical systems with much more efficient energy capacity while maintaining low cost and basic technological characteristics inherent in such systems. One of the perspective solutions to this problem can be the application of the hybrid principle of power sources design, which will be discussed in the following parts.

Table 3. Comparison of the cost of power and energy for perspective electrical energy accumulation and storage technologies.

Type	Power Source Operating Principle	Main Features	Cost of Power, $ kW^{-1}	Cost of Energy, $ kW^{-1} h^{-1}	Source
Solidbatteries	Lead acid	Low cost	3.5–12	75–150	[83,85]
	Nickel-cadmium	High pulse power performance	3–30	100–350	[82,85,87]
	Li-ion	Fast and safe charging unprecedented manufacturability	3.5–80	180–950	[84,85]
Fuel cells	With proton exchange membrane	fast startup, flexibility in input fuel, compact	34–62	600–1500	[82,85,87]
	Melt-carbonate	high fuel utilization and power generation efficiency	40–60	500–650	[85–87]
	Solid oxide	combined heat and power efficiency, long-term stability	25–34	650–850	[82,85,86]
Redox flow batteries	Vanadium	no limit on energy capacity, no penalty for mixing electrolytes	3.5–30	75–100	[82,84,85]
	Iron-chromium	abundance of Fe and Cr resources, low energy storage cost	3.1–28	50–100	[82,84,85]

3. Halogen Hybrid Flow Batteries Perspective Concepts Analysis

3.1. Hybrid Principle Basis

Based on the analysis carried out in Section 2, one can conclude that the indicated weak spot in the design of the electrochemical system can be replaced by another concept. This hybrid device may lose performance in some way, but this change can push a device from completely non-functional to viable in terms of functionality. So, in the case of lithium batteries, the lithium-metal electrode was sacrificed and replaced by lithium-intercalated graphite, which led to a 30% decrease in theoretical energy density, nevertheless making it possible to create a battery with a long-life cycle [88].

In general, a natural consequence of this approach is the free combination of design and chemistry for the cathode and anode half-cells of the electrochemical system in a way to balance the system as much as possible in terms of performance. When doing this optimization, there is no need to stay within the same design or operation principle for the power source: the ability to combine different technologies is the key to obtaining new energy storage devices that simultaneously combine the advantages of capacitors, electrochemical or fuel cells, flow batteries and other technologies.

At present, this approach to the development of new energy sources is used everywhere. Thus, an increase in the energy capacity of a conventional double-layer capacitor with the reversible redox electrochemical processes on the electrode near-surface layer leads to a new type of electrochemical capacitor–supercapacitor [89–94]. The combination of various chemistries of galvanic cells has led to the appearance of lithium-sulfur batteries with outstanding performance in terms of specific energy capacity—a value of more than 500 W h has been experimentally achieved [95–101]. Even higher energy intensity (comparable to the energy intensity of gasoline fuel) is demonstrated by a hybrid of a fuel cell and a lithium-ion battery, a lithium-air battery, where electric current is generated due to oxidation of lithium at the anode and oxygen reduction from the air at the cathode [102–110].

Despite a number of difficulties associated with the use of metal anodes, the choice of catalysts and electrolytes, metal-air electrochemical sources are the prominent result of combining the idea of electrolyte circulating through the system and the design of a galvanic cell, for example, for transport applications [111–120].

The principle of combining various electrochemical approaches can also play a decisive role in solving the problems of traditional fuel cells, where you can sacrifice air oxygen by

replacing it with another reagent (whereas the hydrogen reaction is stored at an anode) because such a replacement immediately eliminates the crucial problems of conventional fuel cells: the high cost of the system due to utilization of platinum and other catalysts, and dissolution of cathode catalyst [121–123].

However, an adequate choice of new oxidizing agent for a hybrid flow battery is an extremely difficult task, since several requirements must be met simultaneously: electrolyte must have a high energy density and its reduction reaction must be kinetically fast to ensure the high energy efficiency of the device. Additionally, all reagents and products of the cathodic reaction must be nontoxic, stable and non-flammable, preferably liquids or gases, since, e.g., solids, pastes and suspensions are often commercially less preferable in flow battery design.

3.2. Halogen Hybrid Flow Batteries

Considering the above-mentioned requisites one can recall the hydrogen-halogen hybrid flow batteries, primarily due to rapid, reversible kinetics, which leads to excellent system performance and the use of inexpensive reagents [11,75,124–126]. In such a system a halogen oxidizer X_2 (for example, Br_2, Cl_2, or I_2) is used in the form of an aqueous solution and hydrogen (H_2) is used as a reducing agent. The potential difference between the halogen and hydrogen electrodes V is equal to the EMF (from 0.54 V for I_2 to 1.4 V for Cl_2). It should be noted that F_2, which is not considered here, has the largest potential difference relative to the standard hydrogen electrode (3.05 V), however, due to technological difficulties in the separation of gaseous fluorine from a mixture of gases, its use is unreasonable due to energy considerations and the problem of materials' compatibility with this reagent.

In this battery the following reactions undergo on electrodes (from left to right—charge mode, from right to left—discharge):

$$2X^- \leftrightarrow X_2 + 2e^- \text{ (at cathode)}, \quad (1)$$

$$2H^+ + 2e^- \leftrightarrow H_2 \text{ (at anode)}, \quad (2)$$

$$2HX \leftrightarrow X_2 + H_2 \text{ (overall reaction)} \quad (3)$$

The protons are transferred from the anode through the membrane into the catholyte (solution in contact with the cathode), whose composition changes inside the discharge unit from X_2 to HX, and the HX solution enters the corresponding reservoir.

The most promising halogens that can be used as oxidizing agents in such a system are Cl_2 and Br_2 because the standard potentials of the corresponding redox couples for these substances are the highest (1.36 V and 1.09 V, respectively, for Cl_2/Cl^- and for Br_2/Br^-). Recently, the interest of researchers has mainly shifted towards the hydrogen-bromine system due to its higher specific power with voltage efficiency of more than 90%, as well as a higher oxidant solubility in an aqueous solution.

A serious disadvantage of hydrogen-halogen systems based on chlorine and bromine is the high toxicity and corrosiveness of the halogen oxidizer, whose concentrated solution must be stored in a tank. Another limitation for these systems is the risk of the catalytic layer degradation on the negative electrode due to halogen crossover through the separator, which should not only provide high selectivity but also have low internal resistance to minimize voltage losses.

The transition from traditional vanadium-based redox flow batteries to hydrogen-bromine hybrid chemistry has led to a significant increase in the power density of flow systems. To date, specific power values of 1.4–1.5 W cm^2 have been experimentally achieved for the H_2/Br_2 system [127,128], while for vanadium redox flow batteries, the highest peak power density for laboratory-scale devices reaches 1.3 W cm^{-2} [129–132]. The researchers develop new concepts and models: Dr. Wlodarczyk recently explored the bromine cathode thermodynamics for hydrogen–bromine chemistry in concentrated solutions [133]. Dr. Ronen proposed the perspective concept of the hydrogen-bromine flow battery, which

does not need separation of the cathode and anode half-cells via proton exchange membrane. He also completed a thorough analysis of the catholyte complexation reaction in homogeneous conditions vs. the efficiency of such a flow battery system [134,135]. Recently Dr. Hou reported a chlorine redox flow battery that reversibly performs electrolysis of NaCl aqueous solution until Cl_2 is generated and transformed into the carbonaceous tetrachloride (CCl_4) [136]. Dr. Fisher and some other scientific groups thoroughly investigated the complexation of bromine with different chemical agents (BCA) in aqueous electrolytes of halogen-containing flow systems. The problem of bromine vapor pressure reduction and halogen storage in the insoluble matter or solid material form is of interest in these works [137–139]. As a result, they showed that bromine can be stored in the fused salt of very high concentrations up to 13.6 M, rushing theoretical energy capacity up to 730 A h L^{-1} [137–139]. Recently this group also measured current densities in the diffusion-limited regime and corresponding current distribution mappings vs. the flow rate values for the H_2-Br_2 RFB [140].

Despite the recent developments in the H-Br_2 battery, the solubility of bromine in water under normal conditions is about 0.21 mol l^{-1} [128]. Hydrogen-bromine systems usually use a mixture of bromine dissolved in water and hydrobromic acid (up to 8 mol l^{-1}) [128], which makes it possible to achieve an energy capacity of about 170 W h kg^{-1} [141], much higher than most common vanadium flow batteries energy density of 20 to 50 W h kg^{-1} [19,34,76,142], nevertheless still much lower than, for example, for lithium-ion batteries [143]. Thus, it can be concluded that, despite promising performance in terms of power density, both vanadium-based compounds and halogens show insufficient solubility in water, which leads to limitations on the value of specific energy capacity.

3.3. Halate Hybrid Flow Batteries

The solution to the problem of the insufficient energy capacity of hydrogen-halogen flow batteries was proposed in 2015 by Yu.V. Tolmachev in [15]—to abandon the use of dissolved halogens in favor of a new family of aqueous multielectron oxidants—solutions of halogen oxoacids.

Lithium bromate $LiBrO_3$, which should be converted at the cathode to lithium bromide LiBr, serves as a promising object of study in [15]. Due to the very high solubility of both substances in water (according to [15] even at room temperature, the concentration of a saturated solution of lithium bromate is about 9 mol l^{-1}, and bromide—more than 10 mol l^{-1}) and the transfer of 6 electrons for bromate-bromide transition results in very high charge densities, more than 1000 A h kg^{-1}, which are more than an order of magnitude higher than similar indicators for other redox flow batteries systems proposed to date.

Other advantages of this oxidizing agent, mentioned in [15], and demonstrated experimentally in [144], are its long-term chemical stability (at moderately low pH), low toxicity of the reagent and product, the utilization of commodity chemicals, low cost per unit of generated electrical energy (due to both a relatively inexpensive reagent and the absence of expensive catalysts for the cathodic reaction, in particular, noble metals), low self-discharge rate and the absence of fire and explosion hazards.

Additionally, in addition to lithium bromate, the use of commercially available sodium bromates with water solubility up to 2 mol l^{-1}, seems very promising [15].

The reason why the bromate anion (as well as other oxohalogenate ions) did not attract attention for applications in electrochemical energy earlier is its low electrochemical activity: on all the studied electrodes, including noble metals, its direct electroreduction reaction at high-rate proceeds at high overvoltages. For the first time, it has been experimentally confirmed that despite the direct electroreduction of bromate anion via heterogeneous reactions cannot be performed without the huge cathode overvoltage, nevertheless, it can be carried out via redox mediator autocatalysis (EC″ mechanism) through a combination of the following bromine reduction reactions:

$$Br_2 + 2e^- \leftrightarrow 2Br^- \text{ (heterogeneous)}, \quad (4)$$

which takes place reversibly even on electrodes without expensive catalysts, with the process of comproportionation in the electrolyte bulk

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \text{ (homogeneous)}, \quad (5)$$

which proceeds at sufficiently high acidity of the solution.

The results of theoretical and experimental studies [145–148] confirmed a number of extremely interesting and unexpected effects: the presence of an anomalous dependence of current density on the intensity of the convective mixing of the solution (which is uncharacteristic of any other known electrochemical mechanisms) combined with an anomalously high cathodic current density of order ~ A cm^{-2} in bromate solutions of the molar concentration range.

Successful confirmation of the developed analytical model predictions with experimental rotating disk electrode data for several solutions of bromate anions in sulfuric and phosphoric acids in the molar range of concentrations is presented in the work [149].

Thus, the quantitative agreement of analytical predictions and experimental data allows us to make the following fundamental conclusions on the kinetics of chemical processe:

- The high reversibility of the electrochemical step (5) of the EC″ mechanism for the bromine/bromide redox couple used in the system, even on carbon electrodes. That is a prerequisite for high current density, sufficient voltage for under load conditions and the specific power of the system;
- Irreversibility of the chemical step (5) of the EC″ mechanism due to sufficiently high solution acidity (acid volume concentration approximately in the molar range);
- The first order of the comproportionation reaction (5) with respect to the anions of bromate and bromide, the second order—with respect to the activity of protons:

$$V = k_0^* \left[a_H\right]^2 \left[BrO_3^-\right] \left[Br^-\right], \; k_0^* = k_0 f_{BrO_3} f_{Br}, \quad (6)$$

- where $a_H = 10^{-pH}$ proton activity (in the form of hydroxonium ions), f_{BrO3} and f_{Br} are activity coefficients of the bromate and the bromide anions, correspondingly.
- The six-electron nature of the electrochemical process (the Br atom changes its oxidation state from +5, which corresponds to BrO_3^-, to −1, which corresponds to Br^-) during the cycle is a prerequisite for ensuring a high specific energy capacity of the system.

Prof. Cho et al. have performed a numerical study of this redox-mediated bromate-based electrochemical energy system focusing on the transient cell behavior analysis and mass transport analysis of the main reagent, which resulted in strengthening the conclusions made above about the prospects of such approaches [150]. The numerical model provided by Dr. Chinannai and Dr. Ju has also demonstrated the beneficial features of the $H_2/Br_2/BrO_3^-$ system, demonstrating the discharge characteristics of an H_2/Br_2 cell with BrO_3^- measured under different C-rates [151]. The bromate system was found to have the innovative features to boost cell performance due to its characteristic autocatalytic reaction to keep regenerating enough reactant for the electrochemical reaction, which may lead to a "no-limiting current condition (i.e., no mass transfer loss)" in well-designed cell and operating conditions.

Thorough research by Dr. Modestov's group showed for 50 cm^2 membrane-electrode assembly of hydrogen-bromate flow battery 0.74 W cm^{-2} power density was reached at the cell voltage 0.7 V while catholyte utilization rate was 0.93 in a single pass through membrane-electrode assembly, see Figures 3 and 4 [144,152]. As a result, based on the high-grade assessments one can conclude that such a system can be of interest to break through the challenging issues in conventional batteries

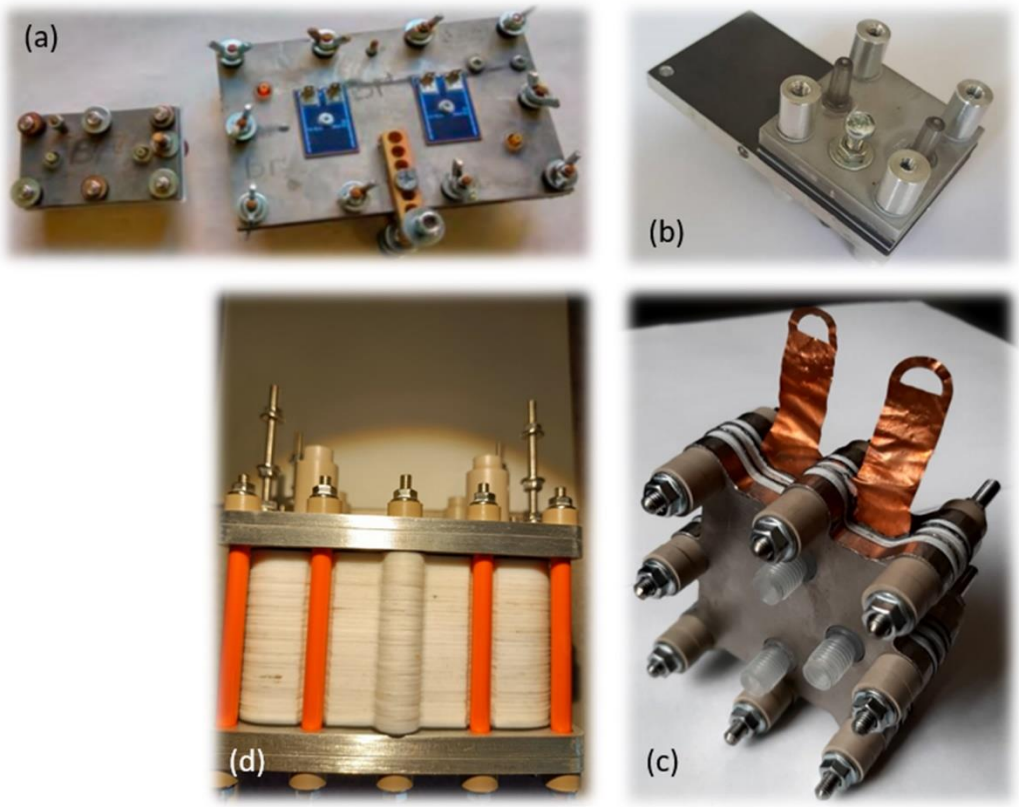

Figure 3. Evolution of hydrogen bromate hybrid flow batteries: Single flow cell (**a–c**): current density I ~ 1.0 A cm^{-2}, power density P ~ 0.7 W cm^{-2}, stack (**d**): I ~ 0.6 A cm^{-2}, power density P ~ 0.3 W cm^{-2} [144,152–154].

3.4. Zinc-Based Halogen Hybrid Flow Batteries

Recalling the high price of vanadium electrolyte, which exceeds USD$ 80/kW h [155,156], one can consider the solid or gaseous phase for positive or negative or even both electrode reactions in the conventional flow battery to switch to the hybrid one. Among hybrid flow systems at the hearing are those based on metal electrodeposition and redox reactions of halogen solution, e.g., zinc-bromine hybrid flow battery, where the reduction of bromine to bromide at the cathode is accompanied by anodic oxidation of metallic zinc. In this case, the reagents are stored in the form of a bromine aqueous solution and a solid zinc coating obtained by galvanization on the surface of the conductive electrode.

Zinc in its pure metal form demonstrated the most enticing energy capacity thanks to its volumetric value (6 Ah cm^{-3}) and high cathodic potential in aqueous solution both in alkaline conditions with −1.29 V vs. SHE or acidic one with −0.76 V vs. SHE [157,158]. Among the other metals suitable for electrodeposition processes in hybrid flow systems the first fiddle plays lead, manganese, iron and chromium. All of them are below 4 $ kg^{-1} since are widely deposited in the earth's core and play important role in the mining industry [159,160]. One can note the more than twice lower price of the electrolyte for zinc-based system (~40 per kW h) vs. sulfuric vanadium one and the most enticing organic electrolyte based on the TEMPO and viologen derivatives—both well above 80 $ per kW h [10].

Moreover, these batteries share the advantages of high voltage and good reversibility, while using low-cost and abundant active materials [161]. The zinc-bromine battery allows the use of only two reservoirs (for electrolytes) and demonstrates energy capacity comparable to lead-acid batteries [162–171]. Nevertheless, bromine is hazardous and needs to be stored in a special way with sequestering agents or in systems with controlled flow, the positive half-cell should be hydrodynamically isolated not only from the negative one but from the external environment to prevent any leak of it [172].

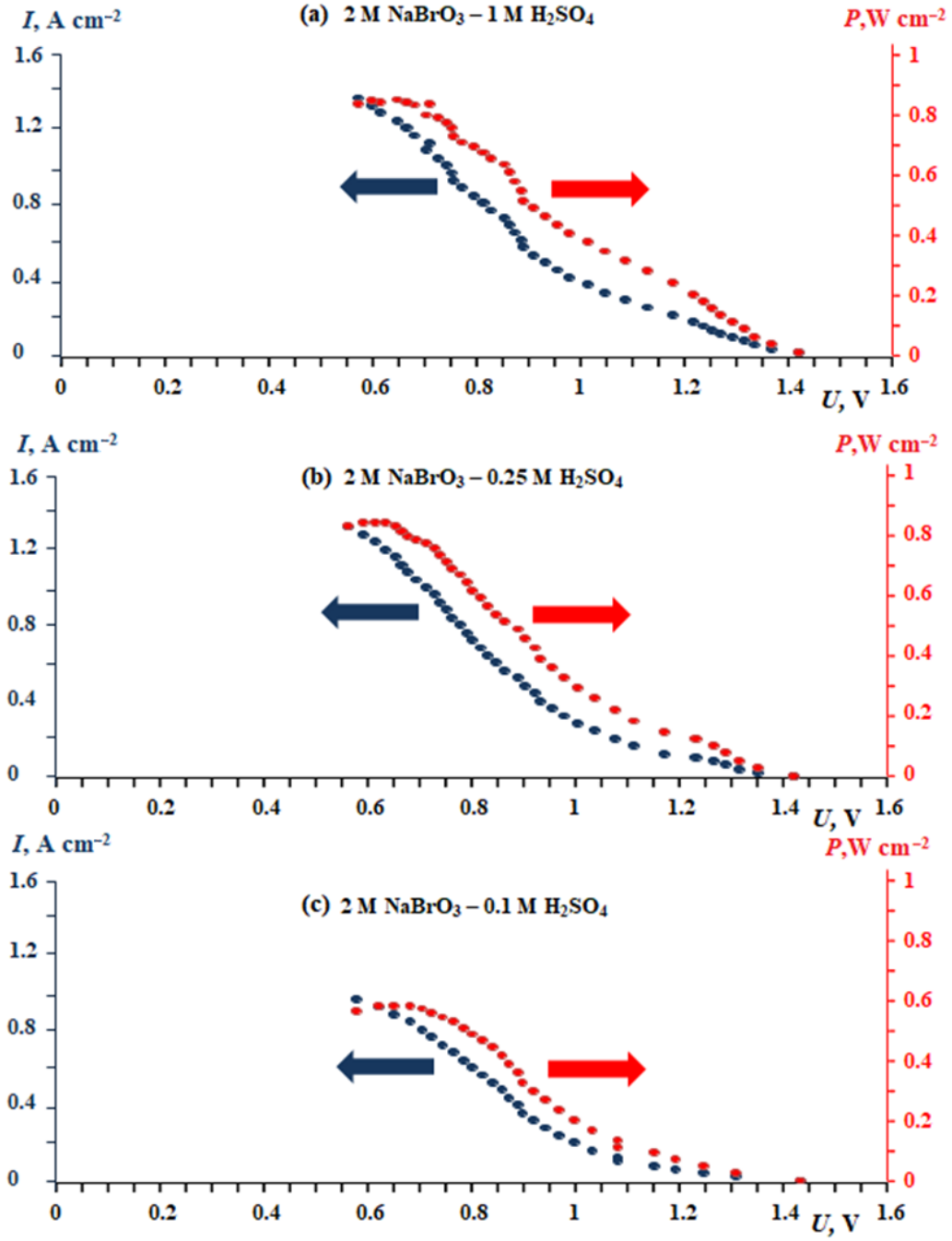

Figure 4. Dependence of current density and specific power vs. voltage for a laboratory membrane electrode assembly prototype (see Figure 3a) with an active surface area of 50 cm^2 at different acidic concentrations of the bulk solution: (**a**) 1 mol L^{-1} H_2SO_4, (**b**) 0.25 mol L^{-1} H_2SO_4, (**c**) 0.1 mol L^{-1} H_2SO_4.

In spite of the low price of zinc-bromine electrolytes, the necessity of the complexing and sequestering agents increases the whole price of the zinc-bromine system up to 350–400 $ per kW h depending on the required energy capacity and stability making it poor competitive with the common vanadium flow batteries in terms of LCOS [85,173]. Moreover, the values of energy capacity in the negative half-cells with zinc electrodes are also limited to 500–1000 mA h cm^{-2}.

Less common analogs of zinc-bromine hybrid flow systems are zinc-iodine, zinc-chlorine and zinc-cerium batteries [174–177]. Zinc-iodide flow batteries (ZIFBs) offer outstanding solubility while the kinetics of the I^-/I_3^- redox couple is rather rapid [178,179].

Dr. Li et al. proposed the first concept of ZIFB emphasizing its huge energy capacity value [180]. The power densities of such a battery on the other hand are the worst among competing hybrid technologies due to the low current densities, while the poor cyclability finishes the unfavorable combination. Later Lu et al. used the complexing bromine agents and improved the energy density of the ZIFB even further [181]. Other groups also expand this approach in the frame of the zinc-bromine battery concept [169]. Nevertheless, the problem of insufficient coordination between bromine and iodine components leads to the overcomplicated charge strategy for I_2 to become fully charged decreasing the specific capacity practically twice vs. the theoretical value of 268 A h L^{-1} [182].

Quite recently, Dr. Xie et al. made a breakthrough by adopting the porous polyolefin separator and several high conductive electrolytes in a novel ZIFB system for grid-scale energy storage which demonstrated improved cyclability at 1000 cycles and a current density of 80 mA cm^2 [183]. Another work by Dr. Zhang et al. demonstrated an all-aqueous Zn–I_2 RFB hybrid system that operates in alkaline media and reaches an energy capacity of 330.5 W h L^{-1}. Today this value is one of the highest energy densities among the all-aqueous hybrid flow systems [184]. One should mention its prominent cyclability over 200 h with 100% coulombic and 70% voltaic efficiencies leading to the value of 70% energy efficiency with 200 W h L^{-1} volumetric energy capacity.

Considering the problem of dendrites in the zinc compartment prof. Xie et al. have developed a self-healing ZIFB, that possesses higher energy capacity and power density, as well as prolonged cyclability [185]. Focusing on the accumulation of zinc dendrites he effectively eliminated the electrolytes precipitation with soluble KI and $ZnBr_2$ as the redox reactants, while the system showed stable operation for more than 1000 cycles over 3 months with an energy density of 80 W h L^{-1}. Moreover, later the stack demonstrated 700 W in 300 cycles experimental test [179].

Another approach tries to make zinc ions more stable by introducing the complexation bromine agents that create cheap and ecologically friendly posolyte and negolyte. To overcome the mentioned above coordination inconsistency that leads to the slow kinetics between zinc and bromine ions one can use a special electrolyte additive to obtain the complexation side process. Adopting $K_3Fe(CN)_6$ as the positive redox species to pair with the zinc anode with $ZnBr_2$ modified electrolyte, prof. Yang et al. demonstrated neutral Zn/Fe flow batteries with $K_3Fe(CN)_6$ additive, that showed prominent efficiencies and cyclability over 2000 cycles. [186].

In general, problems associated with zinc deposition and dissolution, especially in acid media, are summarized by Prof. Arenas et al. in their review work for the four main types of redox flow batteries employing zinc electrodes: zinc-bromine, zinc-cerium, zinc-air and zinc-nickel [187].

4. Challenges and Perspectives

The transition from traditional vanadium-based redox flow batteries to hydrogen-bromine hybrid chemistry has led to a significant increase in power density in flow systems overcoming the first of two fundamental barriers that significantly hinder the development of the direction: insufficient specific power due to small values of exchange currents for heterogeneous redox reactions used in RFB.

The second hindering condition of rather low energy density for flow systems was solved via abandoning the use of dissolved halogens in favor of a new family of aqueous multielectron oxidants–solutions of halogen oxoacids. The latter can effectively participate in the electroreduction process via mediated redox autocatalytic reduction (EC″ mechanism) in an acidic medium in the presence of a trace amount of molecular bromine. For a wide range of systems (both model—rotating disc electrode, microelectrodes and fully functional membrane electrode assembly, MEA) it is analytically substantiated, numerically confirmed and experimentally proved the possibility of achieving high current densities (of the order of A cm^{-2}) and peak powers (of the order of W cm^{-2}) in an aqueous solution of halogen oxoacid (e.g., lithium or sodium bromate). Moreover, several studies emphasize that

autocatalytic reduction of halogen oxoacid is performed in the absence of precious metal catalysts at the cathode due to rapid heterogeneous and homogeneous target reactions in acidic media. As a result, it allows the use of cathodes from carbon materials without precious metals making the system cheaper. Nevertheless, to successfully propagate further with hydrogen-bromate concepts one should pay close attention to the durability of such a system since up to now there is no convincing experimental evidence that these systems are able to be effectively recharged maintaining high energy efficiency calculated for the full charge/discharge cycle.

Zinc hybrid flow batteries have proven to be another promising solution for stationary energy storage. One should admit that remarkable achievements have been shown for ZFBs through wide research on advanced materials for such systems, nevertheless, there are plenty of challenges that still need to be thoroughly investigated to realize the commercialization and industrialization of these devices. The power density, the cycle life and even the energy density need to be further improved. To promote the industrialization of ZFBs, advanced materials with a low cost remain in urgent need.

5. Conclusions

A review of scientific literature data on the main modern chemical power sources technologies, as well as their comparative analysis, was carried out. It is shown that the active and dynamic development of the RFB devices is due to the increasing attractiveness of such systems as applied stationary solutions for the problem of energy accumulation and storage. Due to the high rates of development of the main energy storage technologies in the next five-ten years, we can expect a transition from a centralized to a decentralized energy resources model based on the widespread number of technologies for chemical energy storage with the main representatives shown in Figure 5.

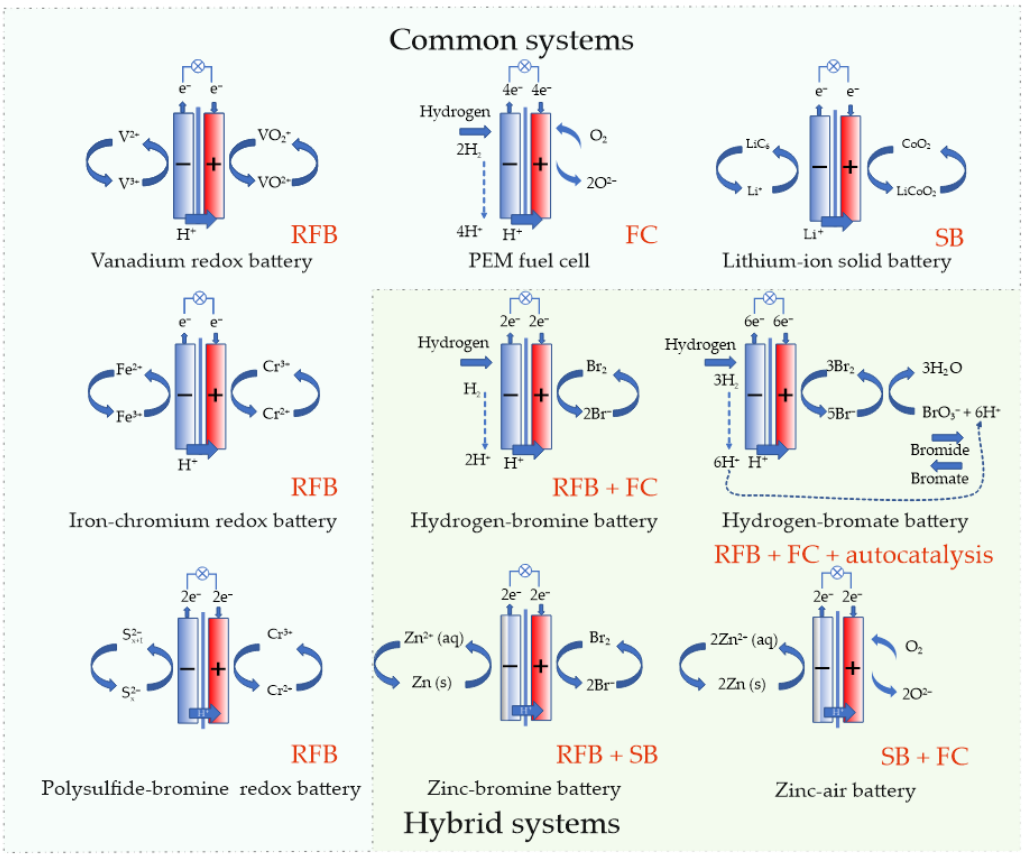

Figure 5. The bias of the flow power sources for electrochemical energy storage applications: evolution from common towards hybrid systems.

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Abbreviations

Acronym or Designation	Definition
CPS	Chemical power sources
DER	Distributed energy resources
EMF	Electromotive force
EPS	Electrochemical power sources
ESS	Energy storage system
FC	Fuel cell
HRFB	Hybrid redox flow battery
MEA	Membrane electrode assembly
RDE	Rotating disc electrode
RFB	Redox flow battery
SB	Solid battery
SDG or SDGs	Sustainable development goal(s)
SHE	Standard hydrogen electrode
VRFB	Vanadium redox flow battery
ZIFB	Zinc-iodide flow battery
ZFB	Zinc flow battery

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